

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 4th, the President, Mr. F. W. F. Arnaud, in the chair.

Certificates were read in favour of Harold Grange Coles, B.Sc., M.A., A.I.C., Alfred Francis Colson, B.Sc., A.I.C., Claude Alexander Dunbar-Mitchell, M.A., A.I.C., Alfred Dudley Husband, F.I.C., George Vaughton James, B.Sc., A.I.C., John Brown McKean, F.I.C., John George Peirce, B.Sc., John Rae, V. Venkatachalam, M.A., Allan Miles Ward, D.Sc., Ph.D., A.I.C.

The following were elected Members of the Society:—Lionel Harry James, M.Sc., A.I.C., and Arthur Jones, M.Sc.

The following papers were read and discussed:—"The Occurrence and Origin of Lead in Canned Sardines," by L. H. Lampitt, D.Sc., F.I.C., and H. S. Rooke, M.Sc., F.I.C.; "The Chemical Examination of Furs in Relation to Dermatitis," Part II, by H. E. Cox, M.Sc., Ph.D., F.I.C.; and "The Investigation of Japanese Beeswax," III, by H. Ikuta.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Manchester on October 14th. The Chairman (Mr. John Evans), presided over an attendance of forty-four.

The following papers were read and discussed:—"Foreign Starch in Arrowroot," by P. H. Jones, F.I.C.; "A Note on Pearl Barley," by P. H. Jones, F.I.C.; and "The Examination of One Thousand Milks by the Hortvet Freezing-Point Process," by J. R. Stubbs, M.Sc., F.I.C., and G. D. Elsdon, B.Sc., F.I.C.

Deaths

WITH deep regret we record the following deaths:

EDWARD THEODORE BREWIS (October 19th).

ALFRED EDWARD JOHNSON, Wolverhampton (September 30th).

JOHN DAVID ROBERTS, Acton (September 25th).

Obituary notices will be published later.

Ancient Egyptian Materials and Industries about 1350 B.C.

By A. LUCAS, O.B.E., F.I.C.

(Address given at the Summer Meeting, North of England Section, June 24, 1933)

THE date, 1350 B.C., is that of the death of Tut-ankhamûn,* whose short reign came almost at the end of the period known to Egyptologists as the Eighteenth Dynasty, a period when the Egyptian empire (not by any efforts of Tut-ankhamûn, but by the conquests of several of his predecessors) included the countries now known as Palestine and Syria, and extended on the north-east beyond the Euphrates as far as the Tigris in northern Mesopotamia.

Before the time of Tut-ankhamûn there had been more than 2000 years of a very high civilisation in Egypt, the date of the great pyramid of Cheops near Cairo, for example, being about 1500 years earlier; and after Tut-ankhamûn there was a period of about 1000 years before the Greek domination (which lasted 300 years). After this came the Roman occupation, which began rather more than 70 years before the Roman conquest of Britain; thus Tut-ankhamûn reigned nearly 1400 years before the history of England began, and the objects illustrated by the slides were approximately 3300 years old.

The materials and industries described—unfortunately only very briefly in the time at my disposal—were stone and stone-working; faience and its manufacture; glass and glass-making; woven fabrics and weaving; wood and wood-working; pigments and varnish with their methods of use, and metals and metal-working.

STONE AND STONE-WORKING.—Egypt is probably the home of stone-working, and it possesses both the oldest and the largest stone buildings in the world. The stone industry dates back to neolithic times (which came to an end probably about 5000 B.C., or some 7000 years ago), during which period small vases were fashioned out of basalt, a fine-grained, black volcanic rock, which, on account of its hardness, is used at the present day for road-making in Cairo. This was the beginning of the wonderful stone-vase industry of the ancient Egyptians, which reached its zenith during the early dynastic period, or some 1900 years before the reign of Tut-ankhamûn, and nowhere has there been found such a wealth of beautifully-made handsome stone vases as in Egypt. The stones used included not only the comparatively soft alabaster, but also such hard stones as diorite, quartz, granite, schist, and volcanic ash. Although the earliest basalt vases were made before copper was known and when only flint tools were available, it was not until the advent of copper that stone-working on a large scale, either for vases or other purposes, was possible, and the great activity in vase-making

* The lantern slides shown during the address (which were kindly lent by Dr. Howard Carter) represented objects from the tomb of this Pharaoh.

and the use of stone for building began only after the invention of copper tools in the late predynastic period (before 3400 B.C.).

The methods employed for obtaining the stone are inferred from the evidence to be seen in the ancient quarries, more particularly where there are blocks only partly detached, though, for a long period after the quarrying of soft stone had become common, some of the hard stones, notably diorite and granite, were obtained from boulders.

The quarrying of soft stone was effected by isolating a block on four sides by means of trenches, and then detaching it from below by the action of wooden wedges or wooden beams, which were wetted with water to expand them after they had been placed in position. The tools employed were metal chisels (at first copper, later, bronze, and still later, iron), wooden mallets and stone hammers.

The quarrying of hard stone consisted essentially in pounding with roughly spherical balls of dolerite (which are found naturally in the desert in certain places) and in the use of wedges.

The method of working the stone after it had been quarried may be deduced partly from the marks left on objects, particularly on statues (of which a large number of unfinished examples are known), but partly also from illustrations of some of the processes that are depicted on tomb walls.

The ancient Egyptian stone statues, especially those in such hard material as diorite, granite, quartzite and schist, have long been a source both of admiration on account of their excellent workmanship, and of wonder and speculation as to the nature of the tools used, and it is still sometimes stated that the working of hard stones could only have been done by means of steel tools and, therefore, that steel must have been not only known, but in common use. This, however, is not so, and the methods employed were as follows:

1. Pounding with a hard stone held in the hand, which is represented in tomb paintings.
2. Rubbing with hard stones held in the hand, which is also represented in tomb paintings.
3. Sawing with a copper blade with the help of an abrasive powder. Cuts, which can only have been made with saws, occur in granite and schist of the pyramid age.
4. Boring with a tubular drill, which was a hollow copper tube, turned either by rolling between the hands or by means of a handle, the drill being used with an abrasive powder. Examples of the holes bored with a drill of this kind, and also of cores from such drilling, are plentiful from the pyramid age.
5. Boring with a crescent-shaped flint fixed in an eccentric handle and provided with two heavy weights. This drill is depicted on tomb walls, being employed for hollowing out stone vases.
6. Drilling with a copper or stone point with the use of an abrasive powder.

In this connection it may be mentioned that too much stress is frequently laid upon the use of chisels, and, although copper chisels were certainly employed for soft stone, they would have been useless for hard stones; moreover, chisels cannot be employed with an abrasive powder. The conditions of the times, too, and the very great patience of the Egyptian workman, are factors that functioned

very largely in the matter, the latter in particular being rarely taken sufficiently into account; and much that is thought to be impossible is only so because the modern workman has neither the time nor the patience to undertake it.

The abrasive powder used was probably very finely-ground quartz sand employed wet, and not emery, as is often stated.

Although the use of stone, including hard stone, for building purposes, for statues, statuettes, and small objects, continued until a very late period, the use of hard stones for bowls and vases died out long before the time of Tut-ankhamûn, this material having been superseded for vessels by faience, glass and copper; there were a large number of stone vases in the tomb, but, with one exception (which was of serpentine) they were all of the comparatively soft alabaster. Everywhere, except in Egypt, alabaster means calcium sulphate, but Egyptian alabaster is always the massive, crystalline form of calcium carbonate (often banded), which is termed calcite by geologists, and which is very like the sulphate in appearance, though somewhat harder.

The word alabaster is derived from *alabastron*, which was the name given by the Greeks to the Egyptian material and, therefore, prior right to the name alabaster seems to belong to the carbonate and not to the sulphate.

FAIENCE AND ITS MANUFACTURE.—Although the term “faience” for this material may not be strictly correct etymologically, and although “glazed siliceous ware” is more in accordance with its composition, it is convenient to retain the conventional name generally employed. The term “glazed pottery” sometimes used is entirely wrong, pottery being ware made from clay, moulded into shape while wet, and then hardened by being baked.

Faience is as old as predynastic times (before 3400 B.C.), and by the early dynastic period it had reached a high standard of excellence, having been used, for example, at the beginning of the Third Dynasty, or about 5000 years ago, in the form of small blue tiles for covering certain walls in the step pyramid at Saqqâra and in a neighbouring large tomb. Its production continued until a very late period, and it was employed for making beads, necklace-pendants, rings, amulets, inlay for coffins and furniture, tiles, bowls, vases, animal and human figures, and for many other purposes.

When a broken surface of faience is examined, the material is seen to consist of at least two, and sometimes of three, different layers—always an inner core with an outer coating of vitreous glaze, but occasionally also an additional thin layer between the core and the glaze, which, when present, is usually very marked on account of the difference in colour and density between it and the core.

The core generally consists of very fine, though occasionally of comparatively coarse, material, frequently white, but almost as frequently slightly tinted blue, green, brown or grey; when examined microscopically it is seen to consist essentially of fine, clean, sharp, angular grains of quartz, and chemical analysis shows it to contain between 94 and 99 per cent. of silica. The material, therefore, is artificially powdered quartz, which may be quartz rock, quartz pebbles or quartz sand, pebbles being the most probable for the very white material and sand for the brownish coarser material. The blue and green colours are due to an admixture of particles of coloured glaze with the quartz, possibly caused by the re-use of old,

broken material. The additional layer, when present, is also quartz, but more finely divided, and hence denser than the core, and the glaze is simply coloured glass.

Small objects were moulded in red pottery moulds, of which many thousands have been found, whilst larger objects were shaped by simple pottery methods, the finer details being added with a pointed tool.

A problem that has perplexed Egyptologists is how such a material as powdered quartz, which is without any natural coherence, was held together while being shaped and glazed. That some binding material was used in small amount seems certain, and this has variously been stated to have been clay, alkalis, lime and organic materials; such as oil, fat, gum, or glue. The use of clay may be disproved both by microscopical examination and by chemical analysis; lime (*i.e.* quick-lime) was not used in Egypt, so far as can be ascertained, before Graeco-Roman times; calcium carbonate (sometimes loosely termed "lime") seems improbable on account of the high temperature required to cause it to combine with the quartz; organic materials have given most unsatisfactory results when tried, though it is difficult to prove that they were not used, since they would probably have burnt out during firing. After experiments had been made with a large number of different materials, the most suitable, and a very likely one to have been employed, was found to be natron, which consists essentially of sodium carbonate and sodium bicarbonate, and occurs naturally and plentifully in Egypt. This, when used in small proportions (from 5 to 10 per cent.) with powdered quartz, forms sufficient sodium silicate to bind the mass together; by varying the proportion of natron any degree of friability or hardness required may be produced. For moulding, the dry powdered natron was mixed with the powdered quartz and pressed into the moulds (which in the experiments made were ancient ones) with the fingers, and for larger objects a strong solution of natron gave the powdered quartz sufficient plasticity to permit of its being shaped by simple pottery methods or by hand modelling. The glaze is of the same composition as the ancient glass, and, although it may be of almost any colour, it is more generally blue or green, the green, however, usually not being original, but due to some chemical decomposition of the blue.

When the body material was a good white the glaze was applied directly, but, when the body was not white and a brilliant blue was required, a thin coating of perfectly white quartz was sometimes put on before the glaze, which may have been done by using a wet mixture of very fine quartz powder and natron and firing. Occasionally, in order to produce a green colour, the secondary layer was coloured yellow by means of yellow ochre, thus causing the blue of the glaze to appear green. The manner in which the glaze was applied is not known, but small objects were probably dipped in the molten glaze and fired. For large objects it has been found that, if powdered glaze be painted on with a solution of gum and fired, the gum burns away, leaving a uniform glazed surface.

GLASS AND GLASS-MAKING.—There can be little doubt that glass was the outcome of glaze; whether the change from the use of glass for covering other objects to its use as a separate material took place in Egypt is uncertain. Glaze was known in predynastic times (before 3400 B.C.), but nearly 2000 years elapsed

before glass was produced regularly on a large scale, although by the reign of Tut-ankhamûn glass-making had reached a high standard of excellence.

Ancient Egyptian glass is essentially a sodium-calcium silicate similar in the nature, though not in the proportions, of its constituents to a modern glass of ordinary quality. The latter, however, contains much more silica, a much smaller proportion of oxides of iron and aluminium, much more lime, practically no magnesia, and much less alkali. The ancient glass, therefore, is softer, more easily melted, and more liable to decay than the modern product.

One of the first uses of glass was for making imitations of precious and semi-precious stones for use as beads and as inlay in jewellery, coffins, furniture, and other objects; thus an opaque light-blue glass was made to imitate turquoise, an opaque dark-blue glass to imitate lapis lazuli, and an opaque red glass to imitate red jasper, and there is little doubt that at this time glass was almost as costly as the stones it simulated. One great difference between ancient and modern glass is that the latter, being so largely employed to transmit light, is transparent, whereas the former, not having been required for that purpose, is generally, at the most, translucent, although more often opaque.

To make the glass, the raw materials, namely, quartz and carbonate of lime (almost certainly generally quartz sand containing carbonate of lime naturally) : alkali, either in the form of natron or of plant ashes (usually the former), and the necessary colouring matter, were put into small crucibles and strongly heated until fusion and combination took place, and the main bulk of the material became homogeneous. In order to know when this point had been reached, small portions of the fused mass were taken out, from time to time, by means of copper pincers, and examined. When finished, the glass was allowed to cool in the crucibles, which were finally broken away, as also were the frothy upper surface (caused by the escape of carbon dioxide and combined water), and the dirty lower surface (due to the sinking to the bottom of impurities and dirt). The lumps of glass thus obtained were broken into smaller pieces, which were softened by heat and rolled into thin round rods or flattened into strips for inlaying and, if necessary, the rods were made still thinner by drawing them out, after again softening. Until a late date beads were made by winding thin threads of glass round a copper wire, which was withdrawn when the glass was cold, but during later (Coptic) times a glass tube was made and drawn out to the required thinness, and then cut into beads. Vases were always formed on a sandy clay core, and they were either moulded or made by coiling round the core thin rods of glass, which had been made plastic by heating and were again heated until the rods coalesced. The foot and handle, if any, were added separately. The variegated glass vases, so typical of the Eighteenth Dynasty, were made by first forming a vase of the colour desired for the background, then embedding in this, while soft, rods of differently coloured glass, which while plastic were dragged up and down by means of copper hooks, in order to produce the wavy effect that is a feature of so many of these vases. Small objects were moulded, and blown glass was not made until the Roman period.

WOVEN FABRICS AND WEAVING.—The art of weaving, which grew out of the simpler plaiting of reeds, rushes and grass to make mats and baskets, dates back

in Egypt to the neolithic period, which probably came to an end about 7000 years ago. The only woven fabrics found in Egyptian tombs until Christian times are of linen, since wool, although used for clothing, was ceremonially unclean, and so Herodotus says, when referring to the Egyptians, "nothing of wool is buried with them." For the same reason the priests were forbidden to wear woollen garments. Cotton, which is a product of India, where it was first used, was not known in Egypt until a late period, and silk not until still later.

Flax-growing and weaving were important industries in ancient Egypt, and are often pictured on the tomb walls, and some of the cloth produced is as fine as anything that can be made to-day. The yarn was spun by hand on a small spindle which dangled by the thread that was being twisted between the palms, and was then woven by women on small hand-loom.

Although dyeing was practised, very little is known about either the nature of the dyes or the process used, although mordanting with alum was certainly known at a late date. Two yellow dyes have been identified, one being the colouring matter from the flowers of *Carthamus tinctorius* (safflower), and the other an iron compound, and, since woad was grown in the country during Greek times, this was doubtless used to produce the blue dye.

WOOD AND WOOD-WORKING.—Egypt is, and always has been, poorly provided with large trees suitable for timber, and wood was one of the earliest imports, chiefly cedar and other coniferous woods from Syria and ebony from the Sudan. The Egyptians, however, were very expert carpenters and joiners, and in the tomb of Tut-ankhamûn, for instance, there were examples of wood joined both by dove-tailing and by means of tongues and grooves, and there was also veneer of one wood on another, chiefly ebony on a local wood; glue was largely employed, and hinges, very like modern hinges, were known and used. The tools included chisels, adzes, toothed saws, bow drills (*i.e.* drills turned by means of a bow), and wooden mallets.

Wooden objects were often gilded by first covering the wood with a thin layer of a special plaster made of whiting and glue, on which the gold leaf was laid. Before applying the gold, however, the plaster was often decorated with elaborate scenes and inscriptions in low relief. For large objects, the wood under the plaster was roughened, and often a layer of coarse canvas was glued on. The gold leaf varied considerably in thickness, but was never as thin as the modern leaf. Occasionally thick gold foil was used for special decoration, and was fastened on by means of small gold rivets.

PIGMENTS AND VARNISH AND THEIR USE.—The freshness and brightness of the old Egyptian tomb and other paintings have often been commented upon, and it is sometimes suggested that the pigments employed were such as do not now exist, and even that their nature is unknown. This, however, is not so, as they have frequently been analysed, and most of them are naturally occurring mineral substances still found in Egypt. The colours employed were black, blue, brown, green, grey, red, and yellow. The black was carbon in some form, generally soot (probably scraped from the outsides of cooking pots), though occasionally powdered charcoal. The blue varied in composition according to the date at which it was used, the earliest blue being azurite (a naturally occurring ore of copper found in

small quantity in Egypt). The principal blue pigment, however, was an artificial frit, which was used as early as the pyramid age, and continued until Roman times. This was made by heating together silica (in the form of either sand or ground quartz pebbles), calcium carbonate (added as powdered limestone when quartz pebbles were used, but probably present in the sand when this was employed), and a copper compound (probably malachite) to produce the blue colour. In order that the colour should be pure blue and not either greenish-blue or green, it was essential that the materials should be practically free from iron compounds, and that the temperature of formation should not vary much from 850° C. Another and much more brilliant blue frit is also known, but only from one (large) specimen, and unfortunately there is no record of where or under what circumstances it was found. Analysis shows this to consist almost entirely of silica (97 per cent.); with very small proportions of alumina, lime, magnesia, and alkalis, coloured with a very small amount of an iron compound and entirely free from either copper or cobalt.

The green pigment was at first malachite (a green ore of copper found in several localities in Egypt), but later a green frit analogous to the blue copper frit already described, and occasionally a mixture of blue copper frit and yellow ochre were used. The red and brown pigments were always natural oxides of iron (ochres, umbers and siennas) until Roman times, when a very ugly pink colour was sometimes employed; this consisted of a lake formed from madder on a base of gypsum. The white pigment was sometimes calcium carbonate and sometimes calcium sulphate. The grey was a mixture of black and white. The yellow, until the Eighteenth Dynasty, some few reigns before that of Tut-ankhamûn, was always yellow ochre, after which period orpiment (yellow sulphide of arsenic) was sometimes used, and, since this does not occur in the country, it must have been imported. Most of the ancient pigments, therefore, were either natural mineral substances or were made from such substances.

Much discussion has taken place as to the nature of the paint vehicle employed. Although certain of the pigments will adhere to some extent if applied dry, the result is not very satisfactory, and others (for example, the blue and green frits) will not adhere at all. The colours, therefore, must have been mixed with some vehicle. In modern practice, this is usually a mixture of boiled linseed oil and turpentine, but oil paint was not known in ancient Egypt even as late as Roman times, and the distilled product termed "spirits of turpentine" was also unknown. Since water is so largely used to-day for distemper, this medium naturally suggests itself, and red and yellow ochres will adhere well to stone and wood without any other medium than water, but this is not the case with the blue and green frits, for which some binding material is necessary and, therefore, it is probable that an adhesive was always used. What this was is not known, but gum, glue and white of egg have all been suggested. The most probable is glue, which was known and used for other purposes from an early date; but the difficulty of proving its presence is considerable, since size (thin glue solution) was probably employed, as it is to-day, before painting, to render the ground less pervious and smoother.

Varnish, in appearance very like modern varnish, was employed from some little time before the reign of Tut-ankhamûn, the basis of this, as in modern

varnish, being resin. Before resin can be applied as a coating to any surface it must be in a more or less liquid condition, and in present-day varnish the resin is generally dissolved in boiled linseed oil, turpentine or alcohol. These materials, however, were all unknown in ancient Egypt, and, moreover, the ancient varnish shows no evidence of oil having been used in its preparation and, though readily soluble in alcohol, it is insoluble in turpentine. There would seem to be two possible methods in which this varnish was applied, both of which it is hoped to try experimentally, though up to the present this has not been done. One of these is to use a natural oleo-resin (which as it exudes from the tree is a thick sticky liquid), warmed so as to reduce the viscosity, and the other is to employ an aqueous solution of the resin. The nature of the ancient varnish resin has not yet definitely been determined, but its solubility in alcohol, its insolubility in turpentine, and the orange-red colour it frequently assumes with age are all suggestive of shellac, and from shellac an excellent water varnish may be made by dissolving it in borax or ammonia. Both these materials, however, were probably unknown in ancient Egypt, but another alkali, namely, natron, was well known, as already stated, and occurs plentifully in the country, though whether a satisfactory varnish can be prepared from shellac by dissolving it in natron has yet to be tried.

A black varnish was also used in ancient Egypt, but this was probably a natural black resin of the nature of a lacquer, such as those that occur in the Far East. These, when fresh, are greyish-white viscous liquids and, on exposure in thin films, dry to a hard, black lustrous surface.

METALS AND METAL-WORKING.—The metals in use in ancient Egypt were copper, gold, silver, iron, lead, and tin, with the alloys bronze, brass (at a very late date), and electrum (a natural alloy of gold and silver), the most important of which may briefly be considered.

COPPER.—Copper, which, unlike gold, is rarely found in nature in the metallic state, but which must be produced artificially from unattractive-looking ores, was yet one of the earliest metals known to man. A green ore of copper (malachite), which occurs naturally in Egypt, both in Sinai and in the eastern desert between the Nile and the Red Sea, was employed as early as about 5000 B.C. for painting round the eyes, cosmetics being as old as vanity, and from this ore the metal may be prepared by a simple process of heating it with charcoal. Metallic copper was known in Egypt in the middle predynastic period (some time before 3400 B.C.); in the earliest graves in which it has been found it was in the form of small objects (rings and needles), and only in later graves were there weapons and tools. That is to say, copper did not appear suddenly in a comparatively highly developed form, as one would expect to be the case had it been imported, but all the stages of evolution from the simplest objects to the more complex have been found in proper sequence. Whether, however, copper was discovered by the Egyptians, or in western Asia, as is sometimes claimed, must be left for the future to decide, as it is chiefly a matter of the correct dating of copper articles from different sources, about which there is still dispute. But, even if the Egyptians did not discover copper, they were certainly among the pioneers in its use. To make copper objects the metal was either hammered or cast, and both welding and soldering were practised.

Bronze, which is an alloy of copper and tin, cannot have been an Egyptian discovery, since tin does not occur in the country, and, also, it was not used in Egypt until about 2000 B.C., which was some time after its use can be proved in western Asia. The advantage of bronze over copper is twofold: first, it is harder than copper, and therefore better adapted for weapons and tools; and secondly, it has a lower melting point than copper, and hence it can be cast more readily and at a lower temperature.

IRON.—Among the objects found in the tomb of Tut-ankhamûn were a few of iron, namely, a dagger, a tiny head-rest, a small amulet mounted in a gold bracelet, and sixteen miniature implements having full-sized handles of some coniferous wood (probably cedar), but with blades so small and thin that they could not even have been used by the boy king to play with, the total weight of all the sixteen being about four grms. It has recently been shown that these were probably magical implements for the ritual ceremony of "Opening the Mouth" of the mummy of the dead pharaoh. Apart from a few pieces of iron of disputed authenticity, the only iron known from Egypt before this date is in the form of a few small beads of the predynastic period (before 3400 B.C.). These have been analysed and found to consist of meteoric iron, and not of iron produced by man from an ore, the difference consisting in the fact that meteoric iron contains a notable proportion of nickel (from 5 to 26 per cent., with an average of between 7 and 8 per cent.), whereas terrestrial iron does not.

Iron was first smelted from its ores in western Asia, probably somewhere south-east of the Black Sea, and it was employed in Asia long before its use reached Egypt, which was not until about 800 B.C., or some 550 years after the time of Tut-ankhamûn. So far as is known, although there are plenty of iron ores in the country, iron was not produced in Egypt, until about Greek times, and then only in small amount.

The chief reason that iron became known to man so much later than copper, although iron ores are far more abundant than copper ores and fairly easily smelted, probably was that iron must be hammered and worked hot, whereas copper can be worked cold, and doubtless metallic iron had often been produced accidentally and tried and rejected as useless until some genius (or possibly merely an impatient person, who could not wait for the material to cool) tried hammering it while still hot, and was amazed at the result.

GOLD.—Owing to its glittering yellow colour, and the simplicity of the treatment required to separate it for use, gold was very early known to man. In Egypt, gold occurs both in quartz rock and also, in the alluvial form, in the beds of dried streams, and, since the extraction from sand and gravel is a simpler process than its extraction from hard rock, it seems probable that the Egyptians, like so many primitive races, began gold mining with alluvial gold.

The gold-bearing region of Egypt lies between the Nile valley and the Red Sea, gold being also found in the northern Sudan. The gold industry was revived in Egypt some years ago; and, although it has now died down again, more than 83,000 ounces of fine gold of a value of over £350,000 sterling, were extracted during the nineteen years from 1902 to 1920 inclusive. Mining was discontinued, not

because the gold was exhausted, but on account of the difficulty and cost of working. The oldest map in the world is one showing a gold-mining region in the eastern desert of Egypt, and dates from about 1300 B.C., or about 50 years after the reign of Tut-ankhamûn.

A detailed and vivid account of the method of gold mining in Egypt during the later period is given by a Greek writer (Agatharchides), who visited the mines in 170 B.C., and states that they were worked by criminals and slaves guarded by foreign soldiers. After the ore was taken from the mine it was broken by hammers into small pieces, then further reduced to the size of peas in mortars, and finally ground to powder with hand-mills, and this powder was then washed on sloping boards with water in order to separate the metal from the matrix, the gold being collected and fused into small ingots.

The native Egyptian gold always contains silver, varying in amount from about 14 to about 23 per cent.; but whether the Egyptians purified their gold or not until a late date is uncertain, though, judging from the analyses of gold objects that have been made, this seems improbable. In the time of Agatharchides, however, the gold was refined by heating it with lead, salt, tin and barley bran. In this description there is nothing to indicate that the silver chloride formed from the silver in the gold by the action of the salt was treated for the recovery of the silver, and almost certainly the silver was lost.

That the Egyptians were expert goldsmiths is abundantly shown by the objects that have survived, and some of their finest work was done as early as about 5000 years ago, as is proved by the objects from the tomb of Queen Hetepheres, the mother of Cheops (who built the large pyramid near Cairo). Notably fine gold work was also done in the Twelfth Dynasty (about 2000 B.C.).

The amount of gold used in ancient Egypt must have been enormous, since in the tomb of Tut-ankhamûn (who was a nonentity among pharaohs, and died young, and whose tomb had been robbed of many solid gold objects) there was a great wealth of gold, including jewellery, a life-size mask of thick beaten gold which covered the head and shoulders of the mummy, and, most amazing of all, a solid gold coffin about six feet long, which weighs 110 kilos. and is engraved both inside and out.

The making of gold leaf; the making of wire by cutting strips of the metal, which were then rounded by hammering; the soldering of gold; inlaying with precious and semi-precious stones and glass (which were cut to size and cemented in place with a mixture of resin and whiting); the production of an artificial bright pink colour on gold; and the casting, embossing and engraving of gold were all commonplace operations at an early date. Some of these processes are depicted on tomb walls, from which it is evident that both long blowpipes (probably hollow reeds tipped with clay) and foot-bellows were employed in the Eighteenth Dynasty to increase the heat of the charcoal fires.

In addition to the industries described, the ancient Egyptians were skilled in the making of plaster; in the extraction of vegetable oils; in the preparation of leather, cosmetics (some perfumed), paper (papyrus) and ink; as also in the fermentation industries, as proved by their beer and wine, all their operations being essentially manufacturing processes, empirical in character and utilitarian in

result. Doubtless, as the result of long practice and many failures, the Egyptian knew how best to choose his materials and what precautions to take in his operations in order to secure the desired results, which, even judged by present-day standards, are often marvellous. Of the art of chemistry, therefore, a very great deal was known, but, so far as the theory was concerned, there is neither evidence nor probability that this was in any way understood.

The Determination of Ethyl Alcohol in Fusel Oil

By JOHN M. MACOUN

PROBABLY the most accurate method for the determination of alcohol in fusel oil depends, in short, on the extraction of the fusel oil with several times its own volume of water to remove the ethyl alcohol, subsequent saturation of the aqueous layer with sodium chloride, washing of the saline solution with petroleum spirit and distillation. A correction for fusel oil in the distillate is made by means of the dipping refractometer (*vide Alcohol*, by Chas. Simmonds, p. 402). A simplified and much used (but much less accurate) modification of this method is the one described in *Allen's Commercial Organic Analysis*, 5th Ed., Vol. I, p. 161.

This determination is of considerable importance for revenue purposes since fusel oil containing not more than 15 per cent. proof spirit, is, in Great Britain and Canada, allowed to be sold free of Excise duty.

A need was felt in this laboratory for a quicker method, and one nearly as accurate as that referred to by Simmonds, while more accurate than that given by Allen. It was, in fact, desired, if possible, so to simplify procedure, that the determination might on occasion be entrusted to gaugers or other persons not trained chemists.

The method evolved by the writer depends on two principles:

1. When fusel oil containing ethyl alcohol and water has been shaken with a saturated solution of potassium carbonate, the upper layer will, within small experimental error, consist of higher alcohols holding in solution an alcohol-water mixture of constant composition. The lower layer will be virtually non-alcoholic. Data on this point were supplied by Nagendra Chandra Nag and Panna Lal (*J. Soc. Chem. Ind.*, 1918, **37**, 290r). They found 94 per cent. of alcohol by volume in the alcohol-water mixture. Experiments made here, however, showed that 93 per cent. was the figure obtained at the usual working temperature of the Ottawa Laboratory, and this figure has been used in calculating the results here given. The proper figure to use in this connection should be independently determined in each laboratory where this analytical method is employed.

2. When such a fusel oil mixture is shaken with a relatively large volume of a saturated solution of sodium chloride, the ethyl alcohol and water will, again

within small experimental error, pass into the saline layer. The amount of higher alcohols which will accompany the ethyl alcohol is reduced to a minimum by saturating the saline solution, before use, with fusel oil free from ethyl alcohol.

The details of procedure finally worked out were as follows:—

1. To 20 ml. of fusel oil placed in a 50-ml. Eggertz tube graduated in 0.1 ml. intervals are added about 5 grms. of solid potassium carbonate. This is then *well mixed* and, if it is found that all the potassium carbonate goes into solution, more is added until some undissolved solid remains in the solution. If too much has been added and no sharp dividing line between the two liquids is seen, sufficient water is added to obtain two distinct layers. After standing till separation is complete, a reading of the upper layer is made. This is fusel oil plus 93 per cent. alcohol (by volume). Let the contraction from 20 ml. be A.*

2. Another 20 ml. portion of the sample is run from a burette into a "tar acid flask" of 225 ml. total capacity, the neck of which is graduated from 0 to 25 ml. in not more than 0.2-ml. intervals. Saturated sodium chloride solution previously saturated with fusel oil (see below) is added till the flask is about three-quarters full. From 4 to 5 ml. of concentrated hydrochloric acid are added, ensuring complete saturation of the aqueous layer with salt and giving a clean, distinct separation. Exactly 5 ml. of petroleum spirit are added, the flask is shaken well, and enough saline solution is added to make the total volume of liquid 225 ml. The flask is again shaken to ensure thorough mixture. After standing until separation into two layers is complete, the flask is gently tapped and rotated to cause any drops of fusel oil clinging to the sides to rise into the neck. When all the fusel oil has risen into the graduated portion of the flask, a reading of the upper layer is taken. Let the contraction from 25 ml. be B.

The percentage of ethyl alcohol by volume in the sample is then:

$$(B - A) \times 0.93 \times 5.$$

The saline solution required for the above determination is prepared by thoroughly shaking together about 1000 ml. of a saturated sodium chloride solution and 50 ml. of commercial fusel oil freed from ethyl alcohol. After standing, the aqueous layer is drawn off into a stock reagent bottle.†

Commercial fusel oil can be sufficiently freed from ethyl alcohol if submitted to the following process:—The "oil" is allowed to stand for five days over solid granular calcium chloride. The liquid (upper layer only if an aqueous layer has formed) is shaken three times in succession with half its volume of a saturated aqueous solution of calcium chloride. The separated fusel oil is then distilled after filtration. The fraction distilling below 95° C. is rejected as possibly containing ethyl alcohol.

The following are typical results obtained by this method on mixtures of

* *Note.*—Chemically pure potassium carbonate should be used rather than a technical grade, as impurities in the latter cause emulsions which make the line of division between the two liquids difficult or impossible to read.

† *Note.*—If crude salt is used, the saturated salt solution should be filtered before use.

known composition, *i.e.* mixtures of known quantities of fusel oil freed from ethyl alcohol with known quantities of ethyl alcohol and water:

Sample No.	Contraction with K_2CO_3 A	Contraction with NaCl B	Alcohol per cent. by volume		Difference per cent.
			Originally present	Found	
1		0.0	0.00	0.00	
2	0.7 ml.	1.9 ml.	5.95	5.58	-0.37
3	1.6 "	4.0 "	11.90	11.16	-0.74
4	2.9 "	7.6 "	23.80	21.85	-1.95
5	5.9 "	16.0 "	47.60	46.96	-0.64
6	1.0 "	2.8 "	8.60	8.37	-0.23

The insufficiency of the method described in *Allen's Commercial Organic Analysis (loc. cit.)* is well illustrated by a determination made on Sample 6 above. The sample was made up to contain 8.60 per cent. of ethyl alcohol by volume; the present method showed 8.37 per cent. and the method according to Allen 4.04 per cent. On the other hand, the method described by Simmonds (*loc. cit.*), showed 8.75 per cent. of alcohol.

Thus the method here proposed gives results nearly as close to the truth as any hitherto in regular use and very much closer than those obtained by the more popular one. It is therefore more fair to the Revenue-collecting authority than is the latter. At the same time, all its errors seem to be in favour of the tax-payer, which is in accord with the merciful spirit of the law and regulations, while they are least in the critical region 8 to 10 per cent. by volume (including 15 per cent. British proof).

The work summarised above was carried out at the suggestion of Dr. Alfred Tingle, Chief of the Customs-Excise Laboratory, to whom the author is much indebted for encouragement and advice. Dr. Tingle wishes it to be stated that, subject to criticism, the method here described will be in future officially adopted in this laboratory for routine determinations.

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The Determination of Cadmium in the Presence of Zinc, in Spelter and in Zinc Ores

BY A. PASS, A.I.C., AND A. M. WARD, D.Sc., A.I.C.

THE usual method for the determination of cadmium in the presence of zinc, *e.g.* in spelter, by precipitation as sulphide, is long and tedious, and no satisfactory rapid gravimetric or volumetric procedure is known. With the object of evolving such a process, we have investigated two types of method, namely, precipitation of cadmium (*a*) as molybdate, and (*b*) by means of certain organic substituted ammonium iodides.

Concerning (*a*), satisfactory determinations of cadmium can be effected from solutions (80 c.c.) containing ammonium acetate (4 grms.), made acid with acetic acid (8 c.c. of 2 *N*). Zinc is not precipitated under these conditions, if alone, but if both cadmium and zinc are present, the results obtained were generally high. Wiley (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 14), while our work on these separations was in progress, published a method closely akin in detail to the one we used for cadmium. He states that metals, other than magnesium and the alkalis, interfere. We find that copper, if present, is always co-precipitated, and lead, as is well known, is precipitated in like circumstances.* Cadmium molybdate is appreciably soluble in solutions containing ammonium chloride, less soluble in the presence of ammonium sulphate, and slightly soluble in solutions containing ammonium nitrate. It is, therefore, amply evident that cadmium molybdate cannot be used for the separations now under consideration.

With regard to (*b*), Evrard (*Natuurwetensch. Tijds.*, 1929, **11**, 191) has described the precipitation of cadmium by means of hexamethylenetetramine allyl iodide as $(\text{CdI}_2)[(\text{CH}_2)_6\text{N}_4, \text{C}_3\text{H}_5]\text{I}$. The precipitate is well crystallised and easy to handle, but precipitation does not appear to exceed 99 per cent. of the theoretical amount (see Mitchell and Ward, *Modern Methods in Quantitative Chemical Analysis*, 1932, p. 20, footnote). Hurd and Evans (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 16) also criticise the method on the grounds that precipitation is incomplete, and that the precipitate occludes excess of the reagent. Berg and Wurm (*Ber.*, 1927, **60**, 1664; *op. cit.*, p. 50) have used β -naphthaquinoline, which in presence of potassium iodide precipitates cadmium as $(\text{C}_{13}\text{H}_9\text{N})_2\text{H}_2\text{CdI}_4$, and give the following results for zinc-cadmium separations:

Taken.	Zn (grms.)	..	1	2	3	4
	Cd (mgrms.)	..	15.37	8.31	2.91	2.07
Found.	Cd (mgrms.)	..	15.27	8.52	3.00	2.34

We obtained the results given in Table I by their process, using the reagent and potassium iodide in considerable excess.

* It is of interest, in connection with the determination of lead as molybdate, that we find cadmium to be co-precipitated under the conditions described by Mellor (*A Treatise on Quantitative Inorganic Analysis*, p. 332) and by Hillebrand and Lundell (*Applied Inorganic Analysis*, p. 183; p. 253).

TABLE I

Taken Zn (grms.)	—	—	—	1	1	5	1
Cd (mgrms.)	9.8	9.8	9.8	9.8	4.9	9.8	19.6
Found Cd (mgrms.)	9.6	10.0	10.0	9.8	5.1	10.0	19.5

EFFECT OF CONCENTRATIONS OF THE REAGENTS.—The following experiments show the influence of the quantities of potassium iodide and of β -naphthaquinoline used on the extent of the precipitation:

(a) Cadmium (9.8 mgrms. in 140 to 150 c.c. of solution) was taken, and 7 c.c. of β -naphthaquinoline (2.5 per cent.) in $N/2$ sulphuric acid were used.

Potassium iodide solution ($N/5$) added, c.c.	10	20	30	30	40		
Cadmium found (mgrms.)	nil	8.9	9.5	9.6	9.8

In experiments (b) and (c), therefore, 40 c.c. of $N/5$ potassium iodide solution were used.

(b) Cadmium, 19.6 mgrms. in 140 c.c. of solution; volumes of β -naphthaquinoline shown below were added.

Volume added c.c.	Excess of reagent Per Cent.	Cadmium found Mgrms.
3.2	25	17.4
3.8	50	18.4
5.1	100	19.7

(c) In view of the solubility of the precipitate, it would appear better to use a measured volume of the reagent in excess, as in the following experiments, rather than a percentage excess as in (b) above.

Volume added c.c.	Excess c.c.	Cadmium added Mgrms.	Cadmium found Mgrms.
8.9	2.5	49.1	48.5
8.9	2.5	49.1	48.4
6.8	5.0	14.7	14.8
8.3	5.0	24.5	24.9
11.4	5.0	49.1	49.3

The last three experiments were carried out on solutions containing 5 grms. of zinc.

The presence of at least 40 c.c. of $N/5$ potassium iodide solution and an excess of 5 c.c. of β -naphthaquinoline (2.5 per cent.) in a total volume of 140 to 150 c.c. gives, therefore, suitable precipitation conditions.

EFFECT OF OTHER ELEMENTS.—Berg and Wurm do not deal with the separation of cadmium from zinc if such metals as copper, lead and bismuth are present, but state that cobalt, nickel, manganese, iron, chromium, aluminium, and magnesium do not interfere, and that tin and antimony are without effect if ammonium oxalate or larger amounts of sodium tartrate are used. Copper, lead, bismuth, arsenic, antimony and tin are the metals precipitated in acid solution by hydrogen sulphide, and are, therefore, the metals from which cadmium and zinc have usually to be separated by the ordinary methods of spelter analysis.

In Berg and Wurm's method, the addition of potassium iodide would presumably precipitate cuprous iodide and lead iodide, and possibly also bismuth iodide or oxyiodide. Test experiments in the presence of these metals were made.

The aqueous solution (100 c.c.), which contained 50 c.c. of 2 *N*-sulphuric acid, 5 grms. of Rochelle salt, and 5 c.c. of a saturated solution of sulphurous acid, was boiled, and 40 c.c. of *N*/5-potassium iodide were added. After standing for one hour, the precipitate was filtered off and washed with a solution prepared from 40 c.c. of *N*/5-potassium iodide, 100 c.c. of water, and a few drops of sulphurous acid. Cadmium was then determined in the filtrate. The results are given in Table II.

TABLE II

Metals present				Cadmium found Grm.
Copper Grm.	Lead Grm.	Zinc Grm.	Cadmium Grm.	
0.1	—	—	0.0245	0.0244
0.1	—	—	0.0098	0.0098
0.1	—	0.5	0.0491	0.0485
0.01	—	3.0	0.0049	0.0052
0.001	—	3.0	0.0098	0.0107
0.1	—	2.0	0.0196	0.0193
—	0.1	1.0	0.0293	0.0298
0.1	0.1	1.0	0.0732	0.0719
0.001	0.1	1.5	0.0104	0.0112
0.01	0.1	1.0	0.0156	0.0160
0.1	0.2	1.0	0.0259	0.0259
0.02	0.01	1.0	0.0104	0.0111
0.05	0.02	1.0	0.0104	0.0104
0.001	0.01	1.0	0.0104	0.0112
0.01	0.01	2.0	0.0259	0.0262

The separation is fairly satisfactory, but results tend to be high, particularly with the lowest concentrations of copper. Variations in the method of precipitation did not improve the results. If bismuth is present, the solution becomes orange-red after addition of potassium iodide, and bismuth could not be precipitated by varying the acidity of the solution; the precipitate which then separates after the addition of β -naphthaquinoline is brown, and causes the cadmium results to be high.

These difficulties were completely overcome by removing the interfering metals by means of iron. The complete procedure is given in the next paragraph, the precipitation with β -naphthaquinoline differing only in a few minor details from that given by Berg and Wurm.

DETERMINATION OF CADMIUM IN THE PRESENCE OF GROUP II METALS AND OF ZINC.—The solution of the metals in 50 c.c. of 2 *N*-sulphuric acid and a few drops of sulphurous acid was boiled, and a few clean iron nails were added. Heating at a temperature just below boiling point was continued for an hour, the bulk being maintained by the addition of water at intervals. The metallic precipitate and lead sulphate, if lead was present in considerable amount, were collected on a sintered-glass crucible, containing a piece of iron wire, and were well washed with cold water.

To the filtrate (100 to 120 c.c.) were added Rochelle salt (5 grms.) and a few drops of sulphurous acid solution, followed by 40 to 50 c.c. of *N*/5-potassium iodide solution and sufficient β -naphthaquinoline (2.5 per cent.) in *N*/2-sulphuric acid

to provide an excess of 5 to 6 c.c. per total volume of 140 to 150 c.c. The liquid, after addition of potassium iodide, may be lemon-coloured, and the precipitate obtained, light brown, owing, probably to a negligible amount of bismuth, not removed by the iron. The precipitate was allowed to settle for one hour, and then collected on a layer of asbestos contained in a sintered-glass or Gooch crucible. It was thoroughly washed with a mixture of 10 c.c. of *N*/5-potassium iodide solution, 10 c.c. of the β -naphthaquinoline reagent, a few drops of sulphurous acid, and 80 c.c. of water, and was dried as completely as possible by suction. Asbestos and precipitate were then transferred to the beaker in which the precipitation was carried out, and ground with 20 c.c. of 2 *N*-ammonia solution. The asbestos and precipitated cadmium compound were then collected in the Gooch crucible, and washed well with ammonia (2 *N*) and water. The filtrate was transferred to a long-necked flask, and rinsed in with hydrochloric acid (2 *N*) in such amount (usually about 100 c.c.) that its concentration at the end of the titration was at least normal, followed by 10 per cent. potassium cyanide solution (5 c.c.) and starch solution. The liquid was then titrated with *M*/40-potassium iodate solution until the blue colour, which first developed, had become first reddish-violet (due to hypiodous acid), and then colourless: 1 c.c. *M*/40 $\text{KIO}_3 \equiv 1.405$ mgrms. of cadmium.

The largest quantity of cadmium which can be handled conveniently is 0.05 gm. With precipitates from 0.03 gm. of cadmium or more, there is danger that decomposition may be incomplete with 20 c.c. of 2 *N*-ammonia; in such cases, therefore, the asbestos pulp was extracted a second time with a little ammonia, and filtered off. The filtrate was neutralised, an equal bulk of 2 *N*-hydrochloric acid was added, and the solution was poured into the main bulk of titrated solution. If necessary, the titration was then continued.

The results obtained by this procedure are set out in Table III.

TABLE III

Zinc Grm.	Copper Grm.	Lead Grm.	Metals present				Tin Grm.	Cadmium Grm.	Cadmium found Grm.
			Bismuth Grm.	Arsenic Grm.	Antimony Grm.				
1	0.001	0.01	0.01	—	—	—	0.0104	0.0102	
2	0.01	0.10	0.02	—	—	0.01	0.0104	0.0103	
1	0.10	0.10	0.01	—	—	0.05	0.0155	0.0157	
1	0.10	0.10	0.05	—	—	0.01	0.0518	0.0510	
2	0.10	0.10	0.10	—	—	0.10	0.0052	0.0054	
1	0.10	0.10	0.10	—	—	0.10	0.0259	0.0269	
1	0.01	0.05	0.05	0.01	0.01	0.05	0.0259	0.0260	
1	0.001	0.05	0.05	0.02	0.02	0.05	0.0208	0.0215	
2	0.05	0.05	0.05	0.05	0.05	0.05	0.0155	0.0155	

THE METHOD APPLIED TO SPELTTERS, ORES, ETC.—Determinations of cadmium in these materials were made, for comparison, by the hydrogen sulphide method and by the above procedure.

Samples were dissolved in sulphuric acid, the concentration of acid was adjusted to be about 3 per cent., and hydrogen sulphide was passed to precipitate Group II sulphides, together with some zinc sulphide. The sulphides were dissolved

in hot hydrochloric acid (sp.gr. 1.1) or in concentrated hydrochloric acid saturated with bromine. Tin was separated, when necessary, by means of nitric acid, and lead was removed as sulphate. The filtrate, made ammoniacal, was decolorised by means of potassium cyanide, and the cadmium and zinc were precipitated with sodium sulphide. The cadmium and zinc were then separated by means of hydrogen sulphide precipitation from solution containing 8 c.c. of hydrochloric acid (sp.gr. 1.1) in a total volume of 150 c.c., the process being repeated (two or three times) until the filtrate was free from zinc. The cadmium sulphide was converted into cadmium sulphate for weighing.

For the β -naphthaquinoline method, the precipitated sulphides were dissolved in hydrochloric acid or in hydrochloric acid and bromine, evaporated just to dryness, taken up in 50 c.c. of 2 *N*-sulphuric acid, and the iron separation and subsequent steps were carried out as described.

Ores containing siliceous matter were dissolved in nitric acid, and the solution was evaporated with sulphuric acid until fumes appeared, and then diluted. Lead sulphate and siliceous matter were filtered off, and the sulphides were then precipitated. The results obtained are given in Table IV.

Results lettered (*a*) refer to the hydrogen sulphide method, and (*b*) to β -naphthaquinoline method.

TABLE IV

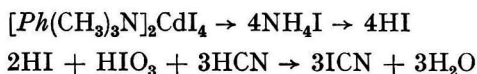
Description	Weight taken Grms.	Cadmium found	
		Grm.	Per Cent.
Spelter A	50	(a) 0.0485	(a) 0.0970
		(b) 0.0488	(b) 0.0976
Spelter B	50	(a) 0.0213	(a) 0.0426
		(b) 0.0218	(b) 0.0436
Zinc oxide	100	(a) 0.0083	(a) 0.0083
		(b) 0.0087	(b) 0.0087
Impure zinc oxide ..	10	(a) 0.0174	(a) 0.174
		(b) 0.0174	(b) 0.174
Blende concentrates ..	10	(a) 0.0143	(a) 0.143
		(b) 0.0148	(b) 0.148
Calamine	10	(a) 0.0178	(a) 0.178
		(b) 0.0184	(b) 0.184

The agreement is eminently satisfactory, but whereas a total time of some 48 hours, involving 10 to 12 hours of manipulation is required for the hydrogen sulphide method, after solution of the sample, the procedure now described occupies about 12 hours with 4 to 5 hours' manipulation. We do not consider the method to possess the highest attributes of a precipitation process, for the complex precipitated is somewhat soluble in water, and it is only by washing the precipitate with a dilute solution of β -naphthaquinoline and potassium iodide that a compensation of errors is achieved. With the object of finding a method free from these possible faults, we are investigating other organic substituted ammonium iodides, and results on phenyltrimethylammonium iodide are given below. This material is very easily prepared, gives a well-crystallised cadmium complex, and allows separations to

be effected as with β -naphthaquinoline; in this case, also, a dilute solution of the reagent in potassium iodide must be used as the washing liquid.

PREPARATION OF PHENYLTRIMETHYLAMMONIUM IODIDE.—Dimethylaniline (13 c.c.) and methyl iodide (7.5 c.c.) were dissolved in chloroform (50 c.c.), and the solution was allowed to stand. After a few days the crystals were filtered off, washed well with chloroform and dried (yield, 26 grms.).

DETERMINATION OF CADMIUM BY MEANS OF PHENYLTRIMETHYLAMMONIUM IODIDE.—Interfering metals were first removed by means of iron, as described under β -naphthaquinoline. To the filtrate was added 3 grms. of potassium iodide, followed by 25 to 30 c.c. of an aqueous solution of phenyltrimethylammonium iodide (2.5 grms. per 100 c.c.). A cream-coloured, well-crystallised precipitate separated. After standing for 6 hours, or preferably over-night, the precipitate had settled and was collected in asbestos in a Gooch crucible or sintered-glass crucible, and was then washed with five successive portions of about 5 c.c. each of a solution of 1 gm. of potassium iodide and 1 gm. of phenyltrimethylammonium iodide in 200 c.c. of water; it was dried by suction as completely as possible after each washing. The precipitate and asbestos were treated with ammonia as in the β -naphthaquinoline experiments, and then transferred, without filtering, to a long-necked flask for titration as already described. The determination depends on the following reactions:



whence, 1 c.c. of $M/40$ $KIO_3 \equiv 1.405$ mgrm. of cadmium. The results given in Table V were obtained with mixtures.

TABLE V

Metals present								Cadmium found Grm.
Zinc. Grms.	Copper Grm.	Lead Grm.	Bismuth Grm.	Arsenic Grm.	Antimony Grm.	Tin Grm.	Cadmium Grm.	
0.25	0.001	0.01	0.01	—	—	0.05	0.0051	0.0059
0.25	0.01	0.02	0.03	—	—	0.05	0.0102	0.0105
0.25	0.10	0.10	0.05	—	—	0.05	0.0153	0.0152
0.25	0.10	0.10	0.01	—	—	0.10	0.0256	0.0258
4.0	0.10	0.10	0.05	—	—	0.05	0.0102	0.0102
4.0	0.001	0.10	0.10	—	—	0.10	0.0204	0.0206
2.5	0.025	0.10	0.07	0.03	0.05	0.05	0.0259	0.0262
1.0	0.025	0.10	0.07	0.03	0.05	0.05	0.0518	0.0514

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The Determination of small Quantities of Nickel in Rock Analysis

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THE procedure usually employed in silicate analysis for the determination of nickel (Hillebrand, *Analysis of Silicate and Carbonate Rocks*, U.S. Geol. Survey Bull. 700; Hillebrand and Lundell, *Applied Inorganic Analysis*, 1929, p. 312) is to separate this element, together with manganese, by means of ammonium sulphide after precipitation of the R_2O_3 oxides with ammonia. This method has several disadvantages; filtration is apt to be tedious, and the known solubility of nickel sulphide in ammonium sulphide leads to incomplete precipitation, whilst the separation of sulphur during the evaporation of the filtrate is troublesome. The assumption is also involved that the whole of the nickel present will be found in the filtrate from the ammonia precipitate, but, as will be shown in the present paper, this is never the case in practice.

The method finally adopted by the authors consists in the determination of the nickel in a separate weighed portion of the rock by precipitation with dimethylglyoxime or with α -fural dioxime.

In view of the statements in the literature, it was thought that it would be possible, as an alternative method, to determine the nickel in the final filtrate obtained after the precipitation of the magnesium as phosphate, and experiments were accordingly made to ascertain if there was any loss of nickel due to its coprecipitation along with the other constituents (silica, R_2O_3 oxides, lime, and magnesia) which had been removed previously; the results indicate that, whilst in some cases a satisfactory determination can be made, the method is decidedly less trustworthy than precipitation of the nickel in a separate weighed portion of the rock.

STANDARD NICKEL SOLUTION.—A solution of 2.241 grms. of pure nickel chloride ($NiCl_2 \cdot 2H_2O$, B.D.H., cobalt- and iron-free) in 7 litres of water containing 10 c.c. of concentrated hydrochloric acid was prepared, and standardised by precipitation with dimethylglyoxime. The results showed that 1 c.c. of the solution contained an amount of nickel equivalent to 0.0000985 gm. of nickel oxide.

PRECIPITATION OF SMALL AMOUNTS OF NICKEL AS GLYOXIME COMPOUND IN PRESENCE OF LARGE QUANTITIES OF SALTS.—Qualitative tests indicated that the presence of ammonium salts, especially the nitrate, in very high concentration, is undesirable where very small amounts of nickel are to be determined. Accordingly, it was found advisable to work with sulphuric acid solutions, and to neutralise the acid, when necessary, with caustic soda. The fact that even small amounts of nickel can be completely precipitated as the glyoxime compound in the presence of a large excess of sodium sulphate was proved by the experiments given below:

Fifty c.c. of the standard nickel solution were treated with 30 c.c. of dilute

(1:1) sulphuric acid and 50 c.c. of water, and the solution was made just alkaline to methyl red by the addition of sodium hydroxide. It was re-acidified with sulphuric acid, 10 c.c. of 1 per cent. dimethylglyoxime solution were added, and then ammonia until just alkaline, followed by a few drops in excess. After standing overnight, the precipitate was filtered off, washed with hot water, re-dissolved in nitric acid, the solution evaporated with a few drops of sulphuric acid, and the nickel again precipitated with glyoxime and weighed.

Weight of nickel precipitate obtained: (1) 0.0192 gm.; (2) 0.0192 gm.

Weight calculated from standardisation of the nickel solution: 0.0191 gm.

CO-PRECIPITATION OF NICKEL AT VARIOUS STAGES IN THE ANALYSIS.—

Silica.—A solution approximating in composition to that obtained in the course of analysis of an average rock was prepared by mixing standardised solutions of the chlorides of iron, aluminium, calcium, and magnesium, and adding 10 grms. of sodium chloride. It contained the equivalent of 0.6 gm. of silica, 0.2 gm. of alumina, 0.15 gm. of ferric oxide, 0.05 gm. of calcium oxide, and 0.20 gm. of magnesium oxide.

Fifty c.c. of the standard nickel solution were added, the liquid was acidified strongly with hydrochloric acid, and the silica was separated by three evaporations in platinum, with intervening filtration in the usual manner. The united silica precipitates, after ignition, were treated with hydrofluoric and sulphuric acids, and the small residue was brought into solution by fusion with potassium pyrosulphate. To the solution of the melt in dilute sulphuric acid a small quantity of citric acid was added, and the solution was almost neutralised with sodium hydroxide. Three c.c. of dimethylglyoxime solution were added, followed by ammonia until the liquid was just alkaline. No precipitate was obtained, even on standing for 24 hours; hence the small amounts of nickel likely to be encountered in rocks do not contaminate the silica obtained by dehydration with hydrochloric acid.

R₂O₃ Oxides.—It is stated in Hillebrand and Lundell (*loc. cit.*) that "practically all of the nickel goes through an ordinary analysis if but moderate amounts are originally present and double precipitations are made throughout. No nickel should be found in the ammonia precipitate." Lundell and Knowles (*J. Amer. Chem. Soc.*, 1923, 45, 676) also state that moderate amounts of iron and aluminium can be separated from nickel as satisfactorily by precipitation with ammonia as by the basic acetate or the barium carbonate methods. Their figures, however, for the separation of 0.05 gm. of nickel from 0.1 gm. of iron or aluminium show some retention of nickel in two out of the four cases given; also the concentration of the iron and aluminium is less than that of the same two elements in an ordinary rock solution. It should be mentioned, however, that these authors were dealing with concentrations of nickel greater than is the case in the present work, and consequently the subject was further investigated to determine whether the co-precipitated nickel was significant in amount. The conditions investigated in this paper correspond more closely with those obtaining in the analysis of silicates, and in all the experiments carried out a co-precipitation of nickel was found to occur.

DOUBLE PRECIPITATION IN THE PRESENCE OF AMMONIUM CHLORIDE.—The composition of the solutions used is shown in Table I.

TABLE I

DATA SHOWING WEIGHTS OF NICKEL CO-PRECIPITATED WITH THE R_2O_3 OXIDES				
Expt. No.	Composition of original solution	Wt. of Ni glyoxime from the filtrate Grm.	Equiv. amount of NiO Grm.	Wt. of NiO corresponding to vol. of standard soln. Grm.
1	10 c.c. standard Ni solution (approx. 0.001 grm. NiO), 0.8 grm. Al_2O_3 , 0.2 grm. Fe_2O_3 , 0.01 grm. TiO (as sulphate), 20 c.c. conc. HCl.	0.0019	0.00049	0.00098
2	10 c.c. of Ni solution, 0.2 grm. Al_2O_3 , 0.3 grm. Fe_2O_3 , 0.01 grm. TiO, and 15 c.c. of conc. HCl.	0.0010	0.00026	0.00098
3	As in Expt. No. 2 with TiO ₂ omitted and 15 grms. of NaCl added.*	0.0019	0.00049	0.00098
4	10 c.c. of Ni solution, 0.2 grm. Al_2O_3 , 0.15 grm. Fe_2O_3 , 15 c.c. conc. HCl, and 15 grms. NaCl.	0.0023	0.00059	0.00098
5	25 c.c. of Ni solution (approx. 0.0025 grm. NiO), 0.2 grm. Al_2O_3 , 0.15 grm. Fe_2O_3 , 15 c.c. conc. HCl, 15 grms. NaCl.	0.0051	0.00132	0.00246
6	As in No. 5.	0.0069	0.00178	0.00246
7	50 c.c. of Ni solution (0.005 grm. NiO approx.), and then as in Nos. 5 and 6.	0.0101	0.0026	0.00492

* Results given below show that sodium chloride does not interfere with the precipitation of nickel by means of dimethylglyoxime.

The method adopted in the precipitation of the R_2O_3 oxides was essentially that recommended by Blum (*Bur. of Stand. Sci. Paper 286, 1916*). The solution containing nickel, iron, aluminium, titanium, and sufficient hydrochloric acid to form moderate amounts of ammonium chloride was diluted to 350 c.c., heated to boiling, and ammonia (1 : 1) added dropwise until the liquid was just alkaline to methyl red. After boiling for 1 to 2 minutes it was again tested with indicator, and filtered while hot, and the precipitate was washed 5 or 6 times with hot 2 per cent. ammonium chloride solution. The precipitated hydroxides were then re-dissolved with the aid of 25 c.c. of concentrated hydrochloric acid, and re-precipitated as before. The united filtrates and washings were combined and evaporated to a small bulk, and the ammonium salts present were removed by treatment with concentrated nitric acid. The excess of nitric acid was removed by evaporation with sulphuric acid, the residue taken up in water, the solution filtered, and the nickel present determined by a double precipitation with dimethylglyoxime as previously described. In three of the experiments, the nickel was determined both in the filtrate and in the hydroxide precipitate, in order to ascertain whether the total nickel originally added to the solution could be recovered. In carrying out the determination of the nickel in the R_2O_3 precipitate, the following procedure was adopted. The second hydroxide precipitate was dissolved completely in dilute sulphuric acid, 1.5 grm. of citric acid was added, and the solution was made just alkaline with sodium hydroxide. It was then acidified again with a few drops of sulphuric acid, and the nickel in this solution was determined by a double precipitation with dimethylglyoxime. The accompanying data (Table II) show that the whole of the nickel originally present was recovered.

TABLE II

Expt. No.	Wt. of Ni glyoxime obtained from (a) R_2O_3 ppt. and (b) filtrate		Sum of (a) and (b) Grm.	Wt. correspond- ing to vol. of standard soln. used Grm.
	(a) Grm.	(b) Grm.		
5	0.0042	0.0051	0.0093	0.0095
6	0.0027	0.0069	0.0096	0.0095
7	0.0089	0.0101	0.0190	0.0190

In order to see if a third precipitation of the R_2O_3 oxides would afford a complete separation from nickel, two further determinations were carried out on solutions similar to those employed in Expt. 5. Three precipitations of the hydroxides were made, and the nickel was determined both in the final precipitate and in the filtrates. The results, given in Table III, show that, although an improved separation results in this way, there is always some nickel retained by the hydroxides. The composition of solutions was the same as in Expt. 5.

TABLE III

Expt. No.	Wt. of Ni glyoxime obtained from (a) precipitate, (b) filtrate		Sum of (a) and (b) Grm.	Wt. correspond- ing to vol. of standard soln. used Grm.
	(a) Grm.	(b) Grm.		
8	0.0008	0.0088	0.0096	0.0095
8a	0.0031	0.0061	0.0092	0.0095

It has been shown by Harwood and Holt (*Min. Mag.*, 1927, 21, 318) that amounts of manganese, up to 50 mgrms. of MnO , present in a rock can be completely precipitated together with the R_2O_3 oxides by the use of bromine water and ammonia without simultaneous co-precipitation of calcium and magnesium oxides. Experiments were therefore made to ascertain what happens to the nickel present when this method is employed to separate the manganese. The solution containing iron, aluminium, nickel, and hydrochloric acid was treated at the boiling point with bromine water and ammonia, added simultaneously, dropwise, the final liquid being just alkaline to methyl red when precipitation was complete. The nickel in both filtrate and precipitate was then determined in the manner previously described. The results (Expt. No. 9), shown in Table IV, indicate that, unlike manganese, nickel is not completely precipitated under these conditions.

TABLE IV

Composition of solution used:—25 c.c. of standard nickel solution, 0.15 gm. of Fe_2O_3 , 0.2 gm. of Al_2O_3 , 5 c.c. of conc. HCl, and water to 350 c.c.

Weight of nickel as NiO in

	1st filtrate Grm.	2nd filtrate Grm.	Precipitate Grm.	
	0.0005	0.0012	0.0007	
Total weight of NiO recovered	0.0024 gm.
Weight of NiO corresponding with 25 c.c. of the standard solution..				0.0025 ..

A second determination (Expt. No. 10) showed a similar irregular distribution of nickel between filtrate and precipitate.

Lime.—Hillebrand and Lundell (*loc. cit.*) state that not more than traces of nickel should be precipitated with the calcium oxalate, and this has been found to be the case. Calcium oxalate was precipitated from a solution containing the chlorides of calcium, magnesium, sodium and nickel as follows:—Two grms. of ammonium oxalate, dissolved in 10 c.c. of water, were added to the above solution (which also contained some free hydrochloric acid)—previously diluted to 200 c.c. The calcium was precipitated by the addition of ammonia (1 : 1) to the boiling solution until it was just alkaline to methyl red. After standing overnight, the precipitate was filtered off, washed with cold 0.1 per cent. ammonium oxalate solution, and re-dissolved in hydrochloric acid; the calcium was then precipitated as before. The second precipitate was washed, ignited to oxide, and dissolved in the minimum amount of hydrochloric acid. The resulting solution was then tested for nickel with dimethylglyoxime as in the previous cases, and the following results were obtained (Table V):

TABLE V

Expt. No.	Composition of solution	Amount of Ni precipitated
11	10 c.c. of Ni soln. (0.001 gm. NiO), 0.15 gm. of CaO, and 5 c.c. conc. HCl.	None
12	25 c.c. of Ni soln., 0.1 gm. CaO, 0.3 gm. of MgO, 15 grms. of NaCl, 15 c.c. of conc. HCl.	Trace
12a	As in Expt. 12	None

Magnesia.—The filtrates from the precipitation of the calcium were acidified with hydrochloric acid, and evaporated to 300 c.c. The magnesium was then precipitated by the addition of 5 grms. of ammonium phosphate, followed by ammonia added slowly, with continual stirring. When precipitation was complete an excess of ammonia was added, and the solution was allowed to stand overnight. The precipitate was filtered off, washed with 2.5 per cent. ammonia, dissolved in hot dilute hydrochloric acid (1 : 10), and re-precipitated after the addition of 0.3 gm. of ammonium phosphate. The liquid was filtered after standing overnight, and the filtrates were united, evaporated to expel ammonia, and freed from ammonium salts by treatment with nitric acid. The nickel was then determined in the usual way after removal of the nitric acid. The results, which are given in Table VI, show that no nickel is carried down with the magnesium ammonium phosphate precipitate. It may be pointed out here that this conclusion is not in agreement with the statement of Hillebrand and Lundell (*loc. cit.*) that the greater part of any nickel will be found co-precipitated with the magnesium precipitate. A point of interest in this connection was revealed in the course of some preliminary work. When solutions of the composition given under Expt. 13, but without the ammonium oxalate, were submitted to the above procedure, no nickel whatever could be found in the filtrate from the magnesium. Hence it appears that in the absence of ammonium oxalate the nickel present is completely precipitated with the magnesium ammonium phosphate.

TABLE VI

Expt. No.	Composition of solution	Wt. of nickel glyoxime recovered Grm.	Equiv. wt. of NiO Grm.	Wt. of NiO corresponding with vol. of standard soln. Grm.
13	10 c.c. of Ni solution, 0.2 gm. MgO, 15 grms. of NaCl, and 2 grms. ammonium oxalate.	0.0036	0.00093	0.00098
14	As in Expt. No. 12.	0.0102	0.0026	0.0025

THE DETERMINATION OF NICKEL IN SILICATE ANALYSIS.—The experiments described above have shown that, owing mainly to co-precipitation with the R_2O_3 oxides, a certain proportion of the nickel present in a rock or silicate never reaches the final filtrate obtained after the successive determination of the silica, R_2O_3 oxides, lime and magnesia. Hence a direct determination of the nickel must be carried out on a separate portion of material. The following experiments showed that small amounts of nickel could be satisfactorily determined by a direct precipitation in the presence of iron, aluminium, calcium, magnesium, and alkalis, citric acid being added to prevent precipitation of the R_2O_3 oxides.

Solutions of the composition given in Table VII were neutralised to methyl red with sodium hydroxide and re-acidified with a few drops of acid, and the nickel was precipitated by the addition of 10 c.c. of 1 per cent. dimethylglyoxime solution, followed by ammonia. It was then weighed as usual after re-precipitation. The results in Table VII show that the nickel is quantitatively precipitated in all cases. In Expts. 15 and 16 sulphuric acid was present, and in 17 hydrochloric acid, whilst in 18 and 19 the hydrochloric acid initially present was removed by two evaporations with perchloric acid prior to the precipitation of the nickel.

TABLE VII

Expt. No.	Composition of solution	Wt. of nickel glyoxime obtained Grm.	Equivalent amount of NiO Grm.	Wt. of NiO corresponding with volume of standard soln. used Grm.
15	25 c.c. Ni soln., 0.2 gm. Al_2O_3 , 0.15 gm. Fe_2O_3 , 10 c.c. of 1 : 1 H_2SO_4 , 1.5 gm. citric acid. Total vol. 120 c.c.	0.0099	0.00256	0.00246
16	As in Expt. 15.	0.0097	0.00251	0.00246
17	25 c.c. Ni soln., 0.2 gm. Al_2O_3 , 0.15 gm. Fe_2O_3 , 0.05 gm. CaO, 0.1 gm. MgO, 1.5 gm. citric acid, 5 c.c. conc. HCl. Total vol. 200 c.c.	0.0094	0.00243	0.00246
18	As in Expt. 17, but with 0.2 gm. MgO.	0.0096	0.00248	0.00246
19	As in Expt. No. 18.	0.0097	0.00254	0.00246

The method finally adopted for the determination of small amounts of nickel in rocks is as follows:—Two grms. of the finely-powdered rock are weighed into a platinum dish, and 15 c.c. of sulphuric acid (1 : 1) are added, followed by 20 to 25 c.c. of pure hydrofluoric acid. The whole is heated on a sand-bath, being kept well stirred during the first 20 minutes or so, to assist disintegration and prevent caking of the powder. When the rock appears to be completely attacked, a crystal of potassium nitrate is added (to oxidise ferrous iron and destroy traces of organic matter possibly present), and the whole is evaporated until the sulphuric

acid fumes strongly, and so maintained for 10 minutes. After cooling, sufficient water is added to dissolve the soluble salts, and the whole is re-evaporated to the fuming point, as before, to ensure complete expulsion of the hydrofluoric acid. The cooled contents of the dish are digested with 100 c.c. of water until all soluble matter has dissolved. The solution is filtered if necessary, and the residue is washed with hot water. As a precautionary measure, any insoluble residue may be ignited in platinum, fused with a little sodium carbonate, the melt taken up with dilute acid, and the resulting solution added to the previous one, but such treatment will rarely be required. Two to 3 grms. of citric acid are added, and the solution is neutralised with sodium hydroxide, methyl red being used as indicator. After re-acidifying with a few drops of dilute sulphuric acid, 10 to 15 c.c. of a 1 per cent. alcoholic solution of dimethylglyoxime are added, followed by ammonia (1 : 3) until an excess of a few drops is present. After standing for 24 to 48 hours the precipitate of nickel glyoxime is filtered off on a Whatman (No. 40) paper, and washed 5 or 6 times with cold water. The washed precipitate is re-dissolved on the filter in the minimum amount of hot (1 : 1) nitric acid, and the filtrate and washings are evaporated as completely as possible on the water-bath after addition of a few drops of (1 : 1) sulphuric acid. The residue is taken up in water, the solution filtered if necessary, and to the filtrate (approximately 50 c.c. in volume) 0.01 gm. of citric acid is added, followed by 5 to 7 c.c. of the dimethylglyoxime solution. This should be added without contact with the stirrer or the sides of the vessel; if this precaution be omitted, small amounts of the precipitant are apt to crystallise on the glass surface, and lead to high results, since it is impossible to remove them in the final washing. Ammonia (1 : 3) is then added, drop by drop, until the solution is just alkaline, followed by 2 to 3 drops (not more) in excess. After standing overnight, the precipitate is collected on a Munro crucible, washed free from sulphate, dried at 120–130° C. for an hour and weighed. The weighed precipitate contains 25.86 per cent. of nickel oxide.

If preferred, 7 to 8 c.c. of 60 per cent. perchloric acid may be used in place of sulphuric acid in the initial attack on the rock powder, but the latter acid has the advantage of removing a good deal of the calcium if much of this element is present, and of effecting a readier expulsion of the hydrofluoric acid.

CORRECTION TO BE APPLIED TO THE ALUMINA ON ACCOUNT OF THE CO-PRECIPIATION OF NICKEL.—As has been shown above, the chief loss of nickel which occurs during the analysis of the portion of rock used for the determination of the silica and main bases takes place through the co-precipitation of this element in the R_2O_3 precipitate. Hence, in accurate work, and when the rock contains more than 0.05 per cent. of nickel oxide, a correction must be applied to the alumina for the nickel oxide present; two methods are available for ascertaining the magnitude of this correction: (a) a direct determination of the nickel precipitated with the mixed oxides, and (b) the determination of the nickel which reaches the final filtrate from the magnesium precipitate. The first method involves a pyrosulphate fusion and is tedious, whilst the second, although not ideal, is easier to carry out and probably just as accurate. This second method consists in the removal of the ammonium salts from the filtrate from the magnesia by means of nitric acid, evaporation to the fuming point with sulphuric acid, and determination

of the nickel present by a double precipitation with dimethylglyoxime, as previously described. The difference between the percentage of nickel oxide thus found, and the total amount present in the rock, as determined in a separate portion, gives the correction to be applied to the alumina.

The magnitude of this correction is indicated by the results shown in Table VIII. These figures were obtained in the course of recent rock analyses made for other purposes. The rocks in question contained relatively large percentages of nickel, and served admirably to apply the methods worked out in the present paper.

TABLE VIII

Rock No.	R_2O_3 oxides			Total NiO, as determined by method given on p. 678 Per Cent.	NiO in filtrate from magnesia Per Cent.	Correction applied to alumina Per Cent.
	Number of pptns.	Total oxides Per Cent.	Al_2O_3 (corrected) Per Cent.			
10293	2	6.68	1.04	0.23	0.18	0.05
10343	3	7.52	0.25	0.23	0.20	0.03
10273	3	7.47	0.66	0.30	0.29	0.01
10335	2	6.91	0.27	0.20	0.19	0.01
14	3	23.73	11.03	0.07	0.06	0.01
3	3	10.77	2.78	0.24	0.21	0.03
4	3	7.75	0.84	0.27	0.24	0.03

SENSITIVITY OF THE METHOD FOR THE DETECTION OF NICKEL UNDER THE CONDITIONS WHICH OBTAIN IN ROCK ANALYSIS.—In rock analysis many of the minor constituents, such as manganese and chromium, can be determined accurately when present to the extent of only 0.01 per cent. It seemed desirable, therefore, to ascertain if the present method for the determination of nickel was equally sensitive, and for this purpose a series of qualitative tests was carried out. Known volumes of the standard nickel solution (previously diluted in some cases to ten times its original volume) were added to a solution similar in composition to that which would be obtained in the course of an analysis made by the method described on p. 678. The resulting solution was neutralised with sodium hydroxide, re-acidified with sulphuric acid, and treated with 10 c.c. of dimethylglyoxime (or α -furyl dioxime) solution, followed by ammonia until just alkaline to methyl red. In all cases the final volume was made up to 200 c.c. The solutions were then examined for precipitation of nickel after a suitable interval of time. The results are given in Table IX.

The tests show clearly that

- (a) α -Furyl dioxime is a more sensitive reagent for nickel than dimethylglyoxime;
- (b) an amount of nickel corresponding with only 0.0025 per cent. of the rock can be detected by means of α -furyl dioxime under the conditions given, and 0.01 per cent. can be readily determined quantitatively by means of dimethylglyoxime.

Where very small amounts of nickel are in question, it is important that no more ammonia should be added during the final neutralisation than is necessary to make the liquid alkaline to methyl red, as an excess tends to hinder precipitation of the nickel compound.

TABLE IX

Composition of solution:—0.20 gm. Al_2O_3 , 0.15 gm. Fe_2O_3 , 0.05 gm. CaO, 0.10 gm. MgO, 5 c.c. conc. HCl, 3 grms. of citric acid, 100 c.c. of distilled water.

No.	Approx. weight of NiO present Mgrms.	Corresponding percentage if 2 grms. of rock are taken for analysis Per Cent.	Observations	Remarks
1	0.1	0.005	Pink stain on filter after 24 hours.	Dimethylglyoxime used.
2	0.1	0.005	No pptn. after 1 week.	" "
3	0.05	0.0025	Faint " turbidity after "	" "
4	0.05	0.0025	Definite ppt. after 24 hours.	α -Furil dioxime used.
5	0.1	0.005	Weighable ppt. after 24 hours.	" "
6	0.2	0.01	Pink stain on filter after 24 hours.	Dimethylglyoxime.
7	0.3	0.015	Weighable ppt. after 24 hours.	" "
8	0.4	0.02	Almost immediate ppt. readily weighable.	" "
9	0.4	0.02	" " " "	" "
10	0.5	0.025	" " " "	" "
11	0.2	0.01	Definite, weighable ppt. after 2 to 3 hours.	Excess of ammonia avoided.
12	0.2	0.01	Ppt. after 5 hours. Definite, after standing overnight.	" "

APPLICATION OF α -FURIL DIOXIME AS A REAGENT FOR THE DETERMINATION OF NICKEL IN ROCK ANALYSIS.—Soule (*J. Amer. Chem. Sec.*, 1925, 47, 981) has pointed out that α -furil dioxime is more sensitive than dimethylglyoxime as a reagent for the detection of nickel, and has applied it to the determination of this element. The qualitative tests described in the previous section (see Table IX) support this conclusion, and on this account α -furil dioxime might well replace dimethylglyoxime as a reagent for nickel when present in small amount. Two quantitative determinations were accordingly made with the furil compound as precipitant, the details of the determinations being otherwise similar to those previously given; the stock nickel solution was also re-standardised, α -furil dioxime being used as precipitant. The results obtained are summarised in Table X.

TABLE X

Weight of nickel α -furil dioxime obtained	Grm.
	(1) 0.0035
	(2) 0.0036
	Mean 0.00355
Equivalent amount of nickel oxide	0.00053
Corresponding weight of nickel oxide according to standardisation with α -furil dioxime	0.00051
Corresponding weight of nickel oxide according to standardisation with dimethylglyoxime	0.00049

The figure for the nickel oxide content is slightly higher by the furil dioxime standardisation than by the dimethylglyoxime method (25 c.c. of nickel chloride solution = 0.00256 gm. of NiO in the first case, as against 0.00246 gm. in the second). The slight solubility of nickel dimethylglyoxime in hot water may be responsible for this, but no importance can be attached to it without further data. The difference is, however, of no significance with the small percentage (0.02 per cent.) involved in the present case. It would seem that the greater sensitivity of

α -fural dioxime makes it a more suitable precipitant than dimethylglyoxime when 0.01 per cent. of nickel oxide has to be determined in a 2 gm.-portion of rock. On the other hand, the reagent is expensive and is difficult to prepare.

SUMMARY.—1. The successive stages of the determination of the main constituents in a rock analysis have been examined for co-precipitation of nickel. It has been shown that this occurs only in the case of the R_2O_3 oxides.

2. Precipitation of the R_2O_3 oxides with bromine and ammonia fails to effect a simultaneous complete precipitation of the nickel.

3. The nickel present can be accurately determined in a separate portion of the rock by precipitation with dimethylglyoxime or α -fural dioxime in the presence of citric acid, the disadvantages of the sulphide method being avoided. A detailed procedure for this is given.

4. The correction to be applied to the alumina percentage for the nickel it contains is discussed.

5. The sensitivity of the method has been examined. Percentages of nickel as low as 0.01 per cent. can be satisfactorily determined by this method, which will also detect the presence of 0.0025 per cent. NiO if 2 grms. of rock are used for the analysis.

6. α -Fural dioxime can with advantage replace dimethylglyoxime as a reagent for nickel when very small amounts are in question, and its use is recommended when amounts of NiO corresponding with less than 0.02 per cent. are to be determined.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF SULPHIDE IN ZINC SULPHIDE BY THE EXPULSION METHOD

STATEMENTS have been made from time to time that the expulsion method for the determination of sulphide in zinc sulphide and lithopones gives low results. Because of the general use and attractiveness of this method, and the ease and rapidity with which it can be carried out, it seemed desirable that these statements should be thoroughly tested by experiment and the reasons for their origin determined.

Different authors have described a number of slight variations in the details of this method, but the essential features are common to them all. The procedure which is considered here, and on which the present work has been carried out, is that given on page 33 of "The Analysis of Paints, Pigments and Varnishes," by J. J. Fox and T. H. Bowles, and is one that has been found very convenient in routine analysis. Hydrogen sulphide is evolved from the zinc sulphide by the

addition of an excess of hydrochloric acid, expelled from the solution by boiling, and swept with a stream of hydrogen or air into an ammoniacal solution of cadmium chloride. The precipitate of cadmium sulphide is then filtered off, washed free from ammonia and added, together with the filter, to a mixture of hydrochloric acid and standard iodine solution. Finally, after shaking for a few minutes, the excess of iodine is titrated with thiosulphate. Throughout these experiments air was used for sweeping the hydrogen sulphide into the cadmium chloride solution, a procedure which, although it is less sound than the use of hydrogen, yet has been found to give results which are sufficiently accurate for most purposes.

Several varieties of zinc sulphide were used in this investigation: a sample purchased as "pure zinc sulphide," a preparation made in this laboratory by precipitation with hydrogen sulphide from a hot solution of zinc acetate in dilute acetic acid, powdered zinc blende and an artificial crystalline zinc sulphide. The method was also used on pure crystals of sodium sulphide, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$.

Those modifications tried were devised to test the various stages of the procedure; to make sure that the hydrogen sulphide can be expelled from the zinc sulphide and caught in the cadmium chloride solution without appreciable loss; to determine if long contact of the cadmium sulphide with the iodine is necessary for their complete interaction, and also if this reaction is reversible.

A summary of these experiments is given in the following table:

Sample used	Wt. taken Grm.	Sulphide found as zinc sulphide		Remarks
			Per Cent.	
Commercial sample of "pure" zinc sulphide.	0.1036	89.5		Standard method.
Do.	0.1000	91.3		Do.
Laboratory preparation.	0.1000	81.3		Do.
Do.	0.1014	80.4		Standard method, but CdS in contact with iodine for $1\frac{1}{2}$ hours.
Do.	0.1002	80.2		Standard method; CdS in contact with iodine for 10 minutes.
Do.	0.1046	83		Sample added direct to acid-iodine mixture.
Do.	0.1022	82		Standard method, but acid added to CdS before iodine.
Do.	0.0550	82		Standard method, but smaller sample taken.
Do.	0.1017	80.5		Sample added direct to acid and dis- solved to clear solution before addition of iodine.
Do.	0.1044	80.5		Standard method, but NaOH solution used instead of CdCl_2 .
		as $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$		
Pure crystals of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$.	0.2511	99		Standard method.
Do.	0.2293	103		Sample added direct to acid-iodine mixture.
		as zinc sulphide		
Powdered zinc blende.	0.1003	96.7		Standard method.
Artificial zinc sulphide crystals (luminescent ZnS).	0.0955	99.7		Standard method.

Since the two crystalline forms of zinc sulphide and the sodium sulphide all gave nearly theoretical values when the proportion of sulphide in them was determined by this method, and since the figures obtained for any one material were always nearly the same whatever slight modification of the procedure was used, it appears that the method is in itself satisfactory, and that the apparently low results obtained for the two samples of zinc sulphide first examined (see Table) are, in fact, true values, both these preparations being deficient in ZnS. A determination of the total zinc and of the total sulphur was made in each of these samples, and each was found to be deficient in zinc sulphide, the commercial

product containing 91 per cent. and the laboratory preparation only 80 per cent. of ZnS. Water was also determined in each sample and the approximate composition of these two products was as follows:

			Laboratory preparation Per Cent.	Commercial sample Per Cent.
ZnS	80.0	91.0
ZnO	11.9	Nil
H ₂ O	7.9	0.25
Free sulphur	..		Nil	6.9
			99.8	98.15

It can therefore be concluded that the method gives substantially accurate results, and that some of the so-called "pure" zinc sulphides of commerce contain only 80 to 90 per cent. of ZnS.

In conclusion, I would like to express my thanks to Dr. J. J. Fox and to Dr. A. G. Francis for their helpful advice and criticism during the carrying out of the work, and also to the Government Chemist, Sir Robert Robertson, for his permission to publish this note.

J. L. BUCHAN

GOVERNMENT LABORATORY
CLEMENT'S INN PASSAGE, W.C.2

THE DETERMINATION OF SMALL AMOUNTS OF BISMUTH IN COPPER

IN the August number of THE ANALYST (p. 475) the Fiscal Policy Technical Sub-Committee of the Brass and Copper Industries give a method for the determination of small amounts of bismuth in copper. At this laboratory we have been engaged on the same problem, and have evolved a method which is essentially similar to that described. There is, therefore, no need to publish our work, but there is one point to which we think attention should be drawn. In the method published by the Fiscal Policy Technical Sub-Committee of the Brass and Copper Industries, sulphurous acid is recommended for reducing the iron to the ferrous condition. It is well known that sulphurous acid produces a yellow colour with potassium iodide (*cf.* Kruisheer, ANALYST, 1932, 57, 672). This colour is identical with the bismuth-potassium iodide colour on which this method depends, and there is therefore this objection to the use of sulphurous acid in the test. For the purpose of reduction, instead of sulphurous acid we have used a solution of stannous sulphate made up in the following manner: Ten grms. of stannous chloride are dissolved in 100 ml. of 6 N sulphuric acid, the solution is allowed to stand, and the clear liquid is poured off for use. Adding from one drop to 5 ml. of this solution makes no difference to the tint of the bismuth colour and gives a colourless blank.

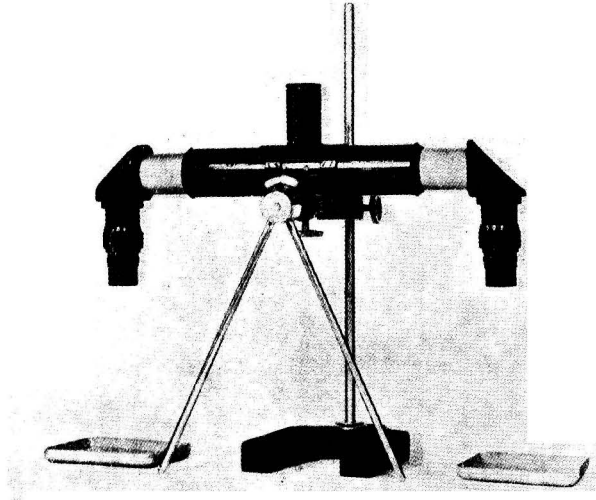
L. C. NICKOLLS

GOVERNMENT LABORATORY
CLEMENT'S INN PASSAGE, W.C.2

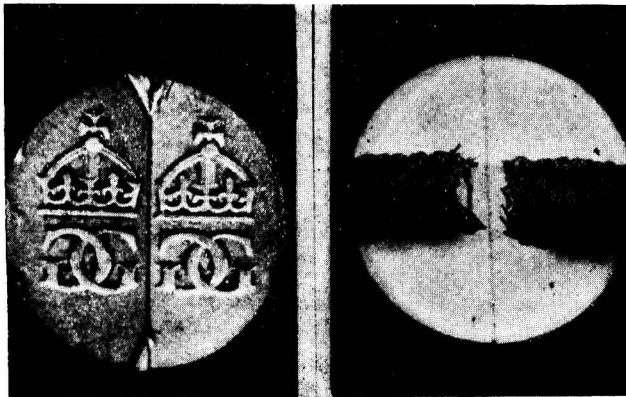
A SIMPLIFIED MICRO-COMPARATOR

THE Micro-Comparator has been devised to facilitate the simultaneous comparison of two objects too large to be brought together in close proximity, for, with its special extension, the instrument covers a range of 30 cm. It thus enables a standard article to be rapidly compared with a sample. Any objects, such as seal impressions, typewritten letters, stamps, paper, textile fibres, wood, etc.,

can be easily compared, and a photographic record made of them with the aid of a micro-camera, which can be fitted to the apparatus.



The instrument, which is mounted on a stand, consists of a telescopic tube which draws out on either side, giving it a range of one foot. In the centre of this tube is one which contains a low-power eyepiece. At either end of the main tube, which is fitted with four specially paired prisms, depends an arm into which low-power magnifiers (*e.g.* $\times 5$) are fitted, and these can be independently focussed. The two halves of the field, viewed through the single eyepiece, appear in juxtaposition.



The ciphers on *two* half crowns placed 12 inches apart.

The cut ends of two pieces of the same flex placed 10 inches apart.

At present the magnification is confined to low powers, but the eyepiece and lenses, being of standard size, are interchangeable with the higher-power eyepieces and objectives ordinarily used on microscopes. The instrument can be adapted to the horse-shoe type of microscope.

Although originally designed to meet certain requirements at the Technical Police Laboratory at Lyons, the apparatus will be found useful for many other scientific purposes. It is made by Messrs. Negretti and Zambra, London, and its name has been provisionally registered as the "Synchriscope."

I am indebted to Dr. Edmond Locard, the Director of the Laboratory, for his critical advice and for permission to publish this note.

LABORATOIRE DU POLICE
PALAIS DE JUSTICE, LYONS, FRANCE

WILLIAM STIRLING

TESTS FOR RE-CONSTITUTED CREAM

IN applying the test previously described (ANALYST, 1928, 53, 334), in which the cream is shaken with a mixture of benzene and methylated spirit (95 per cent. w/v) in equal volumes, further experience has shown that it is better not to give the centrifuge too many turns; sometimes 20 will be quite enough. We generally apply the test to a genuine cream at the same time, and the difference is very marked.

Since devising this test I have used pure acetone. About 5 c.c. of the cream are thoroughly shaken in the centrifuge tube with an equal volume of acetone. After 100 vigorous spins of the centrifuge remarkable differences are to be observed between the two kinds of cream.

- | | | |
|-----------------------|---|--|
| (i) Natural cream. | | No definite separation. |
| (ii) Artificial cream | { from new milk.
made with
skimmed dried
milk. | { A small amber upper layer.
A lower opaque stratum.
A clear liquid with some coagula and
a little sediment as bottom or
fourth layer. |

It is always advisable to test a fresh dairy cream side by side with the article in question.

Contrary to our earlier experience, we find that the method is not very reliable when the cream is turning sour, and the test is therefore best applied to the sample immediately on arrival, particularly in the summer time.

With regard to the test devised by Mr. James Harral (ANALYST, 1933, 605), it should be borne in mind that only with artificial cream in which the milk was prepared from dried milk is the distinctive ratio obtained.

CITY AND COUNTY ANALYST'S OFFICE
BRADFORD

F. W. RICHARDSON

DETECTION OF CHLORIDE IN PRESENCE OF OTHER HALIDES

THE method depends upon the comparative solubilities of the different halides in ammonia solution. The mixed halides are precipitated with silver nitrate, and the precipitate is washed until free from soluble silver salts. The precipitate is then suspended in water, and potassium ferricyanide solution is added, followed by a few drops of dilute ammonia. In the presence of chloride a brownish precipitate of silver ferricyanide is obtained, which is easily visible in the presence of the other halides.

The reaction is extremely simple and is especially useful in the examination of photographic emulsions where the halides are already present in a washed condition.

Care should be taken not to add too much ammonia, and the reaction is, of course, only qualitative.

6 SPENCER GARDENS
EAST SHEEN, S.W.14

WILLIAM BRASH

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE SECOND QUARTER, 1933

OF the 1335 samples submitted by the Food and Drug Inspectors during the second quarter, 1215 were taken informally. Eighty-four of the samples were adulterated or incorrect.

"RICH" CREAM.—Three samples of tinned sterilised cream were described on the labels as "Rich" cream, although respectively containing only 23·5, 25 and 23·5 per cent. of fat. Objection was taken to the term "Rich," since a rich cream should contain about 50 per cent. of fat. In each instance the packers, after some correspondence, agreed to omit the word "Rich" from the label.

IMPLIED ABSENCE OF TANNIN FROM TEA.—A sample of tea bore the label: "All stalks, wherein lies the tannin, have been removed," thus implying that no tannin was present. As a matter of fact, the tea contained 13·6 per cent. of tannin—an average amount. The firm agreed to omit the reference to tannin, and was allowed three months' grace during which the necessary alterations could be made.

COD-LIVER OIL TABLETS.—Reports from the Pharmacological Laboratory of the Pharmaceutical Society on cod-liver oil tablets previously examined showed that, so far as vitamin *A* was concerned, two tablets were equivalent to 1/14 of a teaspoonful of oil of the minimum standard of the B.P., and also that two tablets had only 1/5 the vitamin *D* potency of a teaspoonful of an average sample of cod-liver oil. The label stated that two tablets were equivalent to one teaspoonful of cod-liver oil in respect of both vitamins *A* and *D*, so that the label was definitely a false one. The packers agreed to obliterate the statement on the package and eventually to withdraw the article from the market altogether.

H. H. BAGNALL

CITY OF SALFORD

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1932

OF the 2889 samples examined during the year, 1286 were submitted under the Food and Drugs Act (representing a purchase of 576 samples per 100,000 of population), and of these, 37 were adulterated.

CREAM CHEESE.—Three samples of cream cheese consisted of a soft cheese of the Gervais type. The three samples were similar, containing 29 per cent. of fat and 50 per cent. of water. A detailed analysis showed that, at best, it could not have been made from a mixture of more than one part of cream with nine parts of milk. Since this was a Continental cheese, the makers were given the chance

of altering their label before proceedings were taken against them. In the first instance the makers agreed to withdraw the label and cease using the term "cream cheese" in their advertisements. They afterwards wrote through their solicitors arguing that they were entitled to describe this article as full cream cheese, since this term was widely understood in the trade to mean a cheese made from whole milk. In reply it was pointed out that the real point at issue should be what the purchaser by retail would expect to receive for a soft cheese labelled "full cream cheese." Although no reply to this letter has been received, observation has shown that the sale of this article as cream cheese or full cream cheese has ceased.

CHOCOLATE EASTER EGGS.—A sample, advertised as "Pure Chocolate Cream Easter Eggs," consisted of a cream filling made of sugar, glucose and gelatin coated with chocolate, the thickness of the chocolate amounting to little more than a varnishing. The "chocolate" had to be removed by scraping, and amounted to little more than one-twentieth of the sample. It had, however, a remarkable composition; about three-quarters of the fat (40 per cent.) consisted of a hardened vegetable oil—probably coconut oil—and the remainder consisted of corn flour and cocoa husk.

In view of the relatively small amount of the adulterated part, the maker was asked for interview. He was quite frank about the ingredients used, which he did not make himself. The fatty adulterant was bought as "confectionery butter," and this was, of course, the source of the hardened vegetable oil. He gave an undertaking that he would either coat the Easter eggs with genuine chocolate or cease using the word chocolate in connection with them.

NERVE AND DIGESTIVE TABLETS.—These tablets were manufactured in imitation of a well-known proprietary article, the *modus operandi* of the makers being to issue a pamphlet giving an analysis of the latter, together with the ingredients of their own product. With regard to this sample, both the advertising literature and the label claimed the following ingredients: Potassium iodide, phenolphthalein, calcium sulphate, talc and calcium carbonate. There appeared to be no potassium iodide whatever in the sample, and, since this was, with the exception of phenolphthalein, the only ingredient of marked therapeutic value, the deficiency was serious. Incidentally it may be remarked that potassium iodide is a very expensive ingredient. The manufacturers were asked to appear for interview and gave an undertaking that in future they would take steps to ensure that the labels of their products were in accordance with the composition. A period of six weeks was allowed in which to take the necessary measures.

AMMONIATED QUININE TABLETS.—These tablets were labelled "one drachm," which could only be taken to mean that each tablet was equivalent to one drachm of ammoniated quinine, that is to say, each tablet should contain 1·1/11th grain of quinine sulphate and 6/11ths grain of ammonia. In view of the fact that some difficulty has been experienced by makers of such tablets in preventing loss of ammonia by evaporation, the manufacturers were interviewed, and the reason for the deficiency of ammonia was then obvious. The formula from which the tablets had been made had been calculated to give 1·1/11th grain of quinine sulphate and 0·545 grain of ammonium sulphate per tablet. The opinion was expressed to the manufacturers that these tablets were not the equivalent of ammoniated tincture, not only on account of the deficiency of ammonia, but also because of its presence as a practically neutral salt. The manufacturers agreed to modify their formula accordingly.

COD LIVER OIL EMULSION WITH HYPHOSPHITES.—Eight samples, bought as cod liver oil emulsion with hypophosphites, have been analysed. One of these was actually labelled peptonised cod liver oil emulsion, and its composition corresponded with the B.P.C. formula for this article. It was certified as genuine.

The compositions of the remaining samples disclosed such an interesting state of affairs that the particulars given below:

Vol. of contents Fluid ozs.	Price	Oil Per Cent.	Total hypophosphites Per Cent.	Remarks
	s. d.			
7½	1 3	30·3	0·35	Label claimed 33 per cent. of oil.
6	1 3	23·5	0·3	Label: Oil 25 per cent.
5½	0 11	27·1	0·85	Composition agreed with label.
6	1 3	32·5	0·3	Claimed 33 per cent. of oil.
12	1 6	25·8	0·3	
3½	0 7	57·4	0·9	Label: 50 per cent. of oil.
2½	1 3	40	0·28	Proprietary brand.

Some Published Formulae.

British Pharmaceutical Codex	50	3·66
National Health Formulary	50	3·66
Pharm. J. Formulary Acacia emulsion ..	50	3·0
Pharm. J. Formulary Egg emulsion ..	66	0·6
Pharm. J. Formulary Irish moss emulsion	50	1·14

The recommended dose for adults was the same in each case, viz., one tablespoonful.

A perusal of this list shows at once that manufacturers have all agreed in modifying in some way the accepted formula, and it is a very striking fact that in every case this modification has resulted in the purchaser getting less of the chief medicaments. After interviewing a number of manufacturers, I maintain my original view, that the formula of the Pharmaceutical Codex (which has been followed by the National Health Formulary) represents a reasonable and proper standard for this article. Some of the above samples had to be passed as genuine, since the analyses agreed with the label. Even this does not represent a very satisfactory state of affairs, since the composition was usually expressed in pharmaceutical Latin and on the least conspicuous part of the label. Even if the labels were read, only a pharmacist would appreciate the differences in quality. In interviewing the remaining makers, it was felt that the fairest course was to press for the Codex composition, and, failing that, a proper disclosure on the label as to the actual amounts of oil and hypophosphites present. The various makers agreed to accept one or other of these alternatives. An attempt has also been made to arrive at a more general improvement by asking the National Pharmaceutical Union (representing retail pharmacists) to take the matter up with the makers. A standard for this product would be in the interest of the consumer.

A CASE OF CHRONIC PLUMBISM.—Parts of the organs of a man were submitted by the Coroner. The man, who had been a stereotyper, had had a seizure in 1928, and was then pensioned by his employers. He died in November, 1932. The *post-mortem* findings were cardiac degeneration supervening on general arteriosclerosis, which the pathologist described as being consistent with natural causes or chronic lead poisoning. The organs contained lead in the following amounts:—Liver, 35; brain, 8; kidney, 8; tibia, 27 parts per million. This case is interesting, because of the lapse of four years between the last likely exposure to lead and the subject's death. Taking this into consideration, the amounts present in the body

are very striking. The verdict of the coroner's jury was that the man died from chronic plumbism brought on by his occupation. In course of the examination of the organs a favourable impression was formed of the new method of Allport and Skrimshire (ANALYST, 1932, 57, 440), which was used in addition to the usual processes.

ATMOSPHERIC POLLUTION.—(i) MEASUREMENT OF SUNLIGHT.—The investigation begun in 1926 has been continued, the method used being that described by Bagnall (ANALYST, 1929, 54, 101) and criticised by Moss and Knapp (ANALYST, 1929, 54, 335). Monthly totals (mgrms. of iodine) were recorded, and the following table gives the yearly totals at the four stations for the years 1929 to 1932:

Year	Regent Road	Nab Top Sanatorium, Marple	Ladywell Sanatorium	Drinkwater Park
1932.. ..	1796·7	2123·6	1958·6	1819·1
1931.. ..	1450·6	2084·5	1714·5	1751·5
1930.. ..	1589·7	1895·0	1731·2	1642·2
1929.. ..	1559·0	1932·9	1772·2	1781·5

Considering the figures as a whole, the usual loss of sunlight in the City, as compared with Marple in the country, is very striking. An equally notable feature of the results for 1932 is the higher general totals recorded at all stations, showing the very much better weather with which the year, as a whole, was favoured.

(ii) MEASUREMENT OF ULTRA-VIOLET LIGHT.—An attempt has also been made to measure the comparative variations in intensity of the ultra-violet part of the solar radiation received at the Regent Road Station. The method used was that devised by Dr. J. R. Ashworth, the account of which is reprinted with acknowledgments to its author:—

“It depends on the darkening of self-toning photographic paper on exposure to the ultra-violet light. In order to eliminate all rays but these, the light from the sky is passed through a particular kind of glass called ‘ultra-violet glass’ (obtained from Messrs. Chance Brothers, Birmingham), which has the property of transmitting rays of wave-length round about 3,600 Ångström units, and of excluding all visible light.

“To measure the intensity of the rays after transmission through the glass they are made to pass through a graded wedge of fine tissue paper (known in commerce as ‘9 lb. medium glazed Bank’) made of strips laid one over the other, each strip projecting beyond the last one by 0·3 inches. This wedge has ten strips numbered in Indian ink and is three inches long and about one inch wide.

“The apparatus consists of a shallow light-tight metal box, six inches long, four inches broad, and $\frac{3}{4}$ inch deep, with a strip of ultra-violet glass, $3\frac{1}{4}$ inches by one inch, cemented into an oblong aperture in the lid. The paper wedge is secured behind a slot, the same size as the strip of ultra-violet glass, cut in a piece of millboard which fits into the box and rests on another piece of millboard on which a strip of photographic paper may be laid. Kodak Kodatone self-toning paper has been used in these experiments.

“When observations with the apparatus are to be made, the photographic paper is put on the millboard at the bottom of the box, the paper wedge is superposed in close contact with the photographic paper, the lid closed down and the whole exposed freely to the light of the sky. At the end of a specified time, usually 24 hours, the box is opened, the photographic paper at once examined, and the last number is read off which can just be discerned. This gives the number of layers of paper which the light has penetrated.

“The number so read is the logarithm of the intensity of the light to a first approximation, but in order to test if the logarithmic law may be safely used, some experiments were made in which the layers of paper were placed successively against one face of the photometer, and the transmission factor was then determined for visible light.

“By this photometric experiment, the transmission factors for one, two and three or more layers of paper were found, and by means of the logarithmic law, the transmission factor, f , for one layer of paper was calculated, with the following results:

Layers of paper	n	f
1	0·77
2	0·77
3	0·76
4	0·77
5	0·77

"The uniformity of these results for f shows that it is justifiable to use the logarithmic law. We can, however, if necessary, directly calibrate the scale. When f is known, then a scale of comparative values for I , the intensity of the light, can be constructed for corresponding values of n , the number of layers of paper.

"The transmission factor f_v has been determined as follows for ultra-violet rays: In the first place a piece of fine brass wire gauze was tested for its transmission factor for visible light by means of a Bunsen photometer. Electric glow lamps were placed on either side of the photometer and equality of illumination obtained in the usual way; then one side of the photometer was covered with the gauze, and the lamp nearer the gauze was moved to a new position and equality of illumination again obtained. The lamp on the other side remaining undisturbed; it follows that F , the transmission factor for the gauze, is the ratio of the squares of the distances of the adjustable lamp. In this way it was found that $F = 0.36$. Now this factor must be true for rays which have wave-lengths in the visible or beyond the visible spectrum, and so can be used with ultra-violet light.

"In the next place two identical frames, provided with ultra-violet glass, paper scales and photographic paper, were exposed to the light of an arc-lamp for about 20 minutes. One of the frames was covered with the fine brass wire gauze, and it was found that the light which had passed through the gauze had been reduced in intensity by two steps of the paper scale.

"Now $f_v^n = F$ by the logarithmic law, and as $n = 2$ and $f = 0.36$, it is readily calculated that $f_v = 0.6$.

"Further determinations were made in the same way, using daylight instead of the arc lamp, and the result again was 0.6. This number has been adopted as the transmission factor for ultra-violet light for one layer of paper.

"It will be noticed that this value of f_v for one layer of paper is lower than the value of f found for visible rays, from which it is to be inferred that the paper transmits visible light more freely than the invisible ultra-violet light."

"By recording the number of layers of the paper wedge through which the light has penetrated in any experiment and by using the formula $I = Kf^{-n}$ a comparative measure of the intensity may be obtained. In this formula $I =$ intensity, $f =$ transmission factor for the paper of the wedge (0.6), $n =$ the number of layers penetrated, and $K =$ a constant, arbitrarily fixed as 0.1 for these experiments."

The following table shows the results obtained by this method as monthly totals. It is difficult to give concisely and in simple form an account of results of daily observations having a wide range of variation. The maximum and minimum observations recorded in each month are given, and show the extreme variation experienced during the month:

VARIATION OF ULTRA-VIOLET LIGHT IN SALFORD
REGENT ROAD

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Month, 1932												
Monthly total	326	124	624	1806	2961	4915	2830	1686	1102	600	208	184
Daily max. . .	46	17	46	106	354	354	354	212	128	28	14	14
Daily min. . .	0	0	6	17	17	46	46	6	6	8	4	4
Hours bright sunshine . .	No observations			99.5	81.3	161	100.2	141	89.3	60.5	14.7	5.3

It seems probable that the iodide method tends to give low results in summer, and the photographic method low results in winter.

An extended experience of Dr. Ashworth's photographic method prompts the following evaluation of its merits and defects: Its outstanding qualities are extreme simplicity, cheapness, and the fact that it requires almost no time and attention to operate, and no laboratory or chemical tests. Defects are the discoloration of the paper wedge by sunlight, with the consequent alteration of its transmission factor, and the fact that the process is capable of only a moderate accuracy. The glass filter is comparatively thick, and may cause low readings because it fails to transmit a material percentage of the ultra-violet light falling on it.

It should also be noted that the wave-length of the rays transmitted by the glass filter is about 3,600 Å, while the wave-length of the rays of the greatest medical value is about 3,000 Å. This difference is not serious, and it may be stated with a fair degree of confidence that sound deductions based upon this method for rays of wave-length 3,600 Å will be equally sound for rays of 3,000 Å.

Analysis of the results obtained by the two methods has been made from another angle. If the results obtained throughout the whole of the year are grouped according to the days of the week, it is possible to work out an average value for Monday, Tuesday, etc., and the advantage of this is that, with a fairly large number of Mondays, and so on, variables such as weather tend to cancel out, and we are left with something approaching the ideal week, in the figures for which it may be possible to trace a little of the effect of human activities.

These average figures are given in the following table:

AVERAGE VARIATION OF SUNLIGHT AND ULTRA-VIOLET LIGHT THROUGHOUT THE WEEK, 1932, REGENT ROAD, SALFORD

	Sun. *	Mon.	Tues.	Wed.	Thur.	Fri.	Sat. *
Sunlight	4.45	4.80	5.36	5.08	5.15	5.45	4.45
Ultra-violet light	34	42	57	48	42	53	34

* It is unfortunately impossible to give individual figures for Saturday and Sunday owing to the closing of the laboratory. The figures, identical in each case for Saturday and Sunday, represent half the values obtained by running the experiments over the two days.

Here at once a striking fact emerges. In the City a very material loss of solar radiation, both ordinary visible sunlight and ultra-violet light, occurs at the week-ends, and there is little doubt that smoke produced by the domestic fire is responsible, since industrial smoke must be less at week-ends than at other times. The domestic fire has its peak period at the week-end, owing to the cooking of the Sunday dinner and the use of bigger fires in extra rooms. That Monday is the next worst day is also noteworthy, suggesting that the wind has not completely blown away the heavier pall of smoke produced at the week-ends. Another factor which probably affects the Monday figure is the weekly wash-day, which in so many homes falls on the first week-day.

H. E. MONK

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

ARTIFICIAL CREAM SOLD AS CREAM

ON September 6th a firm of confectioners was summoned at the Pudsey (Yorks.) Police Court for selling "a substance purporting to be cream which was not cream" as defined by the Artificial Cream Act, 1929, and also with manufacturing artificial cream on premises not registered with the County Council for that purpose.

Mr. R. C. Linney, for the Yorkshire County Council, said that an inspector purchased half-a-pint of cream from the defendant company, for which he paid 1s. 6d., which was the price of real cream. The carton was labelled as containing "thick rich cream."

When asked who supplied the cream the defendant had replied: "We make it ourselves." The inspector then asked why he was not told that it was artificial cream, and why it was not labelled as such, and the defendant had replied: "But it is cream, and you can't prove it to be otherwise." The defendant had also stated that they had been manufacturing the substance for about four years, and that it was made from salt-free butter and milk powder. The attention of the defendant was directed to the requirements of the Artificial Cream Act, 1929, and he had said he was not aware of it.

Mr. Linney said that circulars relating to the Act had been distributed among the manufacturers of artificial cream, but he was not prepared to say that the defendant received one. It was quite possible that the firm, which was one of some repute, might have acted in good faith, but it was obviously the defendant's duty to have made himself familiar with the provisions of the Act.

Mr. F. W. Richardson, F.I.C., the County Analyst, said that the substance submitted to him was composed entirely of artificial cream, and, inasmuch as it was sold simply as cream, it was a contravention of the Act. Artificial cream of this kind could be made at a cost of 1s. per pint, and it was usually sold at less than half the price of natural cream. He had never known it sold at as high a price as 3s. per pint.

The defendant said that he could only say that he did not know that he was doing anything that was not perfectly legal. The manufacturers of the machine used to make the cream had told him that the product would stand the analysis of ordinary cream. He had sold it for nearly five years, and he did not know anything more about it than was necessary.

The Magistrates found the cases proved. In the first case the defendants were fined £2 and £1 8s. 6d. costs, and in the second £3 and 10s. 6d. costs.

Report of the Government Chemist upon the Work of the Laboratory

FOR THE YEAR ENDING 31ST MARCH, 1933*

WORK was carried out during the year for the usual Government Departments (*cf.* ANALYST, 1933, 35), and members of the staff were seconded for work in connection with river survey, the Water Pollution Research Board, and the Medical Research Council. The total number of samples examined was 460,995, showing a decrease of 12,060, as compared with the previous year; the number examined at Clement's Inn increased by 3837, and those at Custom House decreased by 13,207, the decrease being almost wholly on imported goods. Samples examined in connection with the General ad Valorem Duty and Additional Import Duties Orders increased (by 4767); the number of samples of tobacco examined for payment of drawback on export, sugar and tea samples also showed an increase, but cocoa, chocolate and wine samples decreased by some 10,000.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter and Margarine.*—Only one of 841 samples of imported butter and 4 of 399 of margarine contained over 16 per cent. of water.

Cheese.—Water varied from 14·3 to 59·1 per cent. in the 115 samples examined, and fat from 1·1 to 38·8, or from 25 to 56·7 per cent. on the dry matter.

Sheep Dips.—Of 37 samples examined, 7 were reported defective.

Sea Water.—Altogether the salinity of 6899 samples was determined, and by this means the drift of water from place to place was followed, since the sea water of the Atlantic is more salt than that of the North Sea. A prepared standard sea water is issued from a central bureau in order that results obtained in different countries should be comparable, and the uniform process followed determines the salinity with an accuracy within one part per 50,000 of sea water. Results from this country are combined with those from other countries and issued from Copenhagen as quarterly advance charts, and yearly in the Bulletin Hydrographique.

Fertilisers and Feeding Stuffs Act, 1926.—Of the 3 fertilisers examined, 2 were mixed, and one was a superphosphate, and the 13 feeding stuffs included meat

* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 9d. net.

meal, meat and bone meals, ground oats, barley, laying and biscuit meals and dry mash. Deficiencies or excesses beyond the limits allowed by the Regulations in oil, protein and/or fibre were found in 3 meat meals, 3 meat and bone meals, laying meal and biscuit meal. Two samples of ground oats contained respectively 40 and 10 per cent. of barley. The dry mash was sold without a statutory statement. The results obtained in the Government Laboratory confirmed those of the agricultural analysts who had examined the samples in the first instance in all cases except three. In one of these the analysis differed by less than 0.2 per cent., but one of the results was just outside the limits of variation allowed by the Regulations, whilst the other was just within. In the case of 2 barley meals the proportions of impurities were estimated as less than 4 per cent., that is within the limit of impurities allowed by the Regulations.

Agricultural Produce (Grading and Marking) Act.—Six of 12 samples of eggs afforded evidence of preservation with sodium silicate. Plain, self-raising, and Yeoman flours were examined; also malt extract, cider and honey samples.

Beer.—The total number of samples examined in connection with duty was 42,642, a decrease of 5443 on the previous year. Of the 105 samples of non-alcoholic beers examined the alcohol ranged from 2 to 6 per cent. of proof spirit in 20 cases. Examination of 1980 samples of beer and brewing materials for arsenic, showed it to be present in slight excess of the limit (1/100th of a grain of arsenious oxide per lb. of solid or per gal. of liquid) in 59 cases.

Cocoa and Chocolate.—The decrease, by nearly 5000, of the samples examined has been partly offset by the fuller examination of the remaining samples necessitated by the Import Duties Act and the Ottawa Agreements Acts of 1932.

Coffee and Chicory.—Fifteen of the imported samples were coffee substitutes composed of roasted cereals or roasted fig.

Dangerous Drugs Act.—Of 50 samples received, 2 consisted of raw opium and one of hashish (Indian hemp), and one preparation contained more than one-fifth of 1 per cent. of morphine.

Hydrocarbon Oils Duty.—Of a total of 7746 samples examined, 3373 were from imported and 2156 from exported goods, and 2683 were hydrocarbon oils and 2851 miscellaneous goods such as enamels, varnishes, etc.

Sikes's Hydrometer.—One hundred and fifty of the new Sikes's "B" hydrometers were examined. These instruments are so devised that by addition of a weight they correspond with Sikes's "A" hydrometers with a range of 66.7 and 73.5 overproof.

Abnormal Importations (Customs Duties) Act, 1931, Import Duties Act, 1932, Ottawa Agreement Act, 1932, and Additional Orders, have involved the examination of 4817 samples, which were of very diverse nature (e.g. fabrics, leather, metals, pigments, rubber goods, pottery, oils, etc.), and have necessitated many difficult analyses.

Spirits.—Of samples for export 2020 were tested for drawback, and the strength of spirit or quantity of sugar was overstated in 125 cases. In 152 cases of 13,627 samples of spirituous preparations for export, the strength of spirit was overstated. Of 55 samples of imported methyl alcohol, 3 were found liable to duty owing to potability. In 27 cases of suspected illicit distillation and grogging 160 samples were examined, and in 12 cases prosecutions were made and convictions obtained.

Sugar.—Examination for sugar or other sweetening matter was made on 74,414 samples, as compared with 71,912 the previous year, and included a very large range of materials.

Tea.—Of 27,959 samples of tea examined, 131 were reported against, representing 360 packages—100 on account of the presence of foreign substances, and 31 as unfit for human consumption.

Tobacco.—Twelve samples of 60 of imported leaf tobacco and 337 of 419 samples of imported manufactured tobacco contained substances not permitted. The percentage of moisture in manufactured tobacco for home consumption was found in 7626 samples, and of oil in 717 samples, whilst 67,427 samples for export were examined. Moisture, inorganic matter and sand were determined in 42,876 samples.

MINISTRY OF HEALTH.—Of 1508 samples of imported dairy produce and 838 samples of other foods, including such substances as pulped fruit, canned vegetables, chocolate, gelatin, cornflour, 39 were reported to the Board of Customs and Excise as contravening regulations. These included 26 samples containing sulphur dioxide, 6 samples containing benzoic acid, 6 containing copper colouring matter, and 1 containing boric acid, either contrary to the Regulations or in excess of the quantities permitted.

FOOD AND DRUGS ACT.—Twelve samples of foods and two of medicines were examined during the year. The foods consisted of six samples of milk alleged to be deficient in fat or non-fatty solids, one sample of egg baking-powder alleged to contain no egg, one whisky below the legal strength, one mince alleged to contain excess of sulphur dioxide, two butters stated to contain excess water, and one jam alleged to be deficient in fruit. The medicines were deficient, respectively, in bismuth carbonate and salicylic acid. In nine cases the results were in agreement, and in four cases in disagreement with those put forward by the prosecution. In one case it was neither possible to determine the inevitable loss of sulphur dioxide during storage nor to state the proportion present in the sample when it was purchased, since some loss must have occurred during the time which elapsed before the sample was submitted for test. One butter contained 15.9 per cent. of water, which is not in excess of the legal limit, one milk was found not to be below the presumptive standard of the Sale of Milk Regulations, and in the case of the jam the proportion of fruit present was not inconsistent with "full fruit standard," having regard to the natural variations in the composition of fruit. In the case of the sample of egg baking-powder, dried egg was found to be present, but in a very small proportion—about 1 per cent.

D. G. H.

The Strength of Spirits Ascertainment Regulations

THE Commissioners of Customs and Excise, in pursuance of the Finance Act, 1907, and paragraph 11 of the Excise Transfer Order, 1909(a), have made the following Regulations:

1.—(i) The following means may be used for the purpose of ascertaining the strength of spirits:—

The specific gravity of the spirits shall be determined and the strength of the spirits shall be taken to be the percentage of proof spirit corresponding in the deposited Tables to the specific gravity of the spirits as so determined.*

For the purpose of the foregoing provision:

The expression "Specific gravity" means the ratio between the weight of a given volume of the spirits at a temperature of 80° Fahrenheit and the weight of an equal volume of water at the same temperature; and

* Cf. p. 723.—EDITOR.

The expression "deposited Tables" means certain Tables entitled "Tables showing the relation between the Specific Gravity of Spirits at 80°/80° Fahrenheit, the corresponding Percentage of Proof Spirit, and the Percentage of Alcohol by Weight," a copy of which has been signed by the Chairman of the Commissioners of Customs and deposited in the Office of the King's Remembrancer.

- (ii) Where the specific gravity of any spirits determined as aforesaid falls between any two consecutive numbers appearing in column I of the Tables, an amount bearing the same proportion to the difference between the two numbers in column II corresponding to the two said numbers in column I, as the difference between the said specific gravity so determined and the lesser of the said two numbers in column I bears to the difference between the said two numbers in column I shall be deducted from the greater of the said two numbers in column II, and the amount so deducted shall be deemed to be the strength of the spirits.

- 2.—These Regulations shall come into force on the eleventh day of September, 1933, and may be cited as the Strength of Spirits Ascertainment Regulations, 1933.

Trinidad and Tobago

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1932

THE Government Analyst (Mr. H. S. Shrewsbury) reports that 3158 samples were examined during the year. Of these, 1828 were for the Constabulary and 413 for the Customs Department. The Food and Drugs Ordinance is administered by the Constabulary, and prosecutions are instituted by the Inspector-General of Constabulary and the Chief Preventive Inspector. Of the 1541 samples of foods submitted, 547 were of milk, 686 aerated drinks, 102 oil, and 99 lard.

COFFEE ADULTERATED WITH ROASTED PEAS.—A sample of coffee contained 21 per cent. of a starchy product foreign to coffee, and found to consist of roasted pigeon peas. This is the first occasion on which coffee has been found to be adulterated in Trinidad. The adulteration was skilful, the product having the normal appearance and odour of genuine coffee. The vendor was fined £3 and costs.

SACCHARIN IN SWEET DRINKS.—The Order prohibiting the adulteration of sweet drinks with saccharin came into force on January 1st, 1932, and in the course of the year 489 samples were analysed, and 37 were found to contain saccharin in amount ranging from 0.0009 to 0.05 per cent. (average 0.0134 per cent.).

DANGEROUS DRUGS ORDINANCE.—One hundred and nineteen samples of opium pipes, parcels with white powder, opium scales, etc., were analysed for the purposes of the Ordinance. Prosecution by the Preventive Officers resulted in fines amounting to £1100 being imposed.

One case has some psychological interest, for a person, who might have been a defendant, was so convinced that he was in possession of morphine that he made a confession to that effect. On analysis, the substance was found to be anhydrous quinine. In another case a sample of supposed opium was free from opium. The attempted sale was fraudulent in view of the high price of illegally sold opium, but no offence had been committed under the Dangerous Drugs Ordinance.

British Pharmacopoeia, 1932

THE following corrigenda are given by permission of the General Medical Council:

CORRIGENDA IN THE FIRST ISSUE (SEPTEMBER, 1932)

<i>page line</i>			
xxxi 44	<i>for</i> Erythritolis	<i>read</i> Erythrytilis	
xxxvi 25	<i>for</i> Rubrum	<i>read</i> Rubri	
14 11	<i>for</i> Tests	<i>read</i> Test	
14 11	<i>for</i> , dissolved in 200 millilitres of <i>water</i> ,	<i>read</i> of a 0.5 per cent. v/v solution in <i>water</i>	
16 29	<i>for</i> parts	<i>read</i> part	
51 24	<i>for</i> 1 gramme, boiled with <i>water</i> until all the ammonia has been driven off, complies with the <i>limit test for iron</i> .	<i>read</i> Boil 1 gramme with <i>water</i> until all the ammonia has been driven off, and add 5 millilitres of <i>dilute nitric acid FeT.</i> ; the solution complies with the <i>limit test for iron</i> .	
52 20	<i>for</i> 2.5 grammes, boiled with <i>water</i> until all the ammonia has been driven off, complies with the <i>limit test for iron</i> .	<i>read</i> Boil 2.5 grammes with <i>water</i> until all the ammonia has been driven off, and add 5 millilitres of <i>dilute nitric acid FeT.</i> ; the solution complies with the <i>limit test for iron</i> .	
54 2	<i>after</i> 90 per cent.	<i>insert</i> w/w	
57 28	<i>for</i> 0.1669	<i>read</i> 0.01669	
63	<i>after</i> line 22	<i>insert</i> The number of Units placed in each container must be sufficient to ensure that the number stated on the label is still present at the end of the period during which the preparation is intended to be used.	
65 33	<i>for</i> <i>talc.</i>	<i>read</i> <i>talc,</i>	
77 4	<i>for</i> <i>Synonyms</i>	<i>read</i> <i>Synonym</i>	
87 13	<i>for</i> determined as	<i>read</i> determined on the alcohol-soluble matter from 5 grammes by the method	
104 33	<i>for</i> 13	<i>read</i> 1.3	
106 18	<i>for</i> 0.02 per cent. w/w	<i>read</i> 0.002 per cent. w/w	
113 24	<i>after</i> <i>hydroxide</i>	<i>insert</i> , prepared with <i>alcohol (95 per cent.)</i> ,	
131 28	<i>for</i> Colchicum Seed	<i>read</i> the colchicum seed being assayed	
163 14	<i>after</i> <i>sulphate . . .</i>	<i>insert</i> 40 millilitres of the filtrate represents 16 millilitres of the liquid extract of colchicum being assayed.	
164 3	<i>after</i> below	<i>insert</i> , commencing with the words 'wash the residue into a separator . . .'	
164 14	<i>for</i> Semen	<i>read</i> <i>Cornus</i>	
164 15	<i>delete</i> about		
173 38	<i>after</i> per cent.	<i>insert</i> v/v	
176 33	<i>after</i> per cent.	<i>insert</i> v/v	
179 17	<i>after</i> per cent.	<i>insert</i> v/v	
192 20	<i>delete</i> dilute		
192 20	<i>for</i> 1	<i>read</i> 0.1	
192 22	<i>after</i> produced	<i>insert</i> immediately	
211 5	<i>for</i> Mercuric Oxide	<i>read</i> Yellow Mercuric Oxide	
226 6	<i>for</i> 2 to 4 mils. 30 to 60 minims.	<i>read</i> 2 to 8 mils. 30 to 120 minims.	
265 17	<i>for</i> <i>water</i>	<i>read</i> <i>alcohol (90 per cent.)</i>	
272 29	<i>for</i> 1 $\frac{1}{3}$ grains	<i>read</i> 1 grain	
297 10	<i>after</i> Oculentum Physostigminæ	<i>insert</i> . <i>Synonym. Oculentum Eserinæ</i>	
324 18	<i>after</i> when	<i>insert</i> dried,	
324 19	<i>after</i> hours	<i>insert</i> (limit of solid paraffins)	
326 40	<i>for</i> Soft Paraffin, white	<i>read</i> White Soft Paraffin	
326 41	<i>for</i> Soft Paraffin	<i>read</i> White Soft Paraffin	
352 9	<i>for</i> 5	<i>read</i> 50	

<i>page line</i>			
352	36	<i>before filter</i>	<i>insert</i> previously neutralised to <i>phenolphthalein</i> ,
352	36	<i>before alcohol</i>	<i>insert</i> neutralised
379	29	<i>after substance</i>	<i>insert</i> ;
381	12	<i>for the ether</i>	<i>read</i> freshly redistilled <i>ether</i>
381	22	<i>for limit</i>	<i>read</i> absence
384	2	<i>for</i> It contains not less than 98 per cent. of the pods described below.	<i>read</i> It contains not more than 2 per cent. of other organic matter.
389	10	<i>for</i> 10	<i>read</i> 20
389	23	<i>after</i> grammes	<i>insert</i> , dissolved in 25 millilitres of <i>dilute nitric acid Fe T.</i> ,
391	25	<i>after</i> grammes	<i>insert</i> , dissolved in 15 millilitres of <i>dilute nitric acid Fe T.</i> ,
394	18	<i>for</i> 5	<i>read</i> 50
395	17	<i>for</i> 5	<i>read</i> 50
428	21	<i>for</i> $\frac{1}{120}$	<i>read</i> $\frac{1}{130}$
443	14	<i>after sulphate</i>	<i>insert</i> 40 millilitres of the filtrate represents 160 millilitres of the tincture of colchicum being assayed.
445	11	<i>for</i> temperture	<i>read</i> temperature
450	3	<i>for</i> represent	<i>read</i> represents
461	16	<i>for</i> Tests	<i>read</i> Test
461		<i>after</i> line 18	<i>insert</i> Tests for Purity. Complies with the <i>tests for sterility.</i>
468	15	<i>for</i> <i>Tuberculosis</i>	<i>read</i> <i>tuberculosis</i>
468	34	<i>for</i> <i>Tuberculosis</i>	<i>read</i> <i>tuberculosis</i>
470	21	<i>for</i> Soft Paraffin	<i>read</i> White Soft Paraffin
471	8	<i>for</i> Soft Paraffin	<i>read</i> Yellow Soft Paraffin
473	19	<i>for</i> Soft Paraffin, yellow	<i>read</i> Yellow Soft Paraffin
485	29	<i>for</i> <i>extract</i>	<i>read</i> <i>extractive</i>
514		<i>after</i> line 20	<i>insert</i> for N/2 . . . 28.05 grammes KOH
535	last	<i>for</i> millimetres	<i>read</i> millilitres
539	39	<i>for</i> No. 118	<i>read</i> No. 188
579	27	<i>for</i> N/10	<i>read</i> N/2
581	2	<i>for</i> millilitres	<i>read</i> millimetres
581	15	<i>for</i> 5	<i>read</i> 3
616	31	<i>for</i> biological	<i>read</i> biological
621	6	<i>for</i> millitres	<i>read</i> millilitres
621	7	<i>for</i> represent	<i>read</i> represents
621	10	<i>for</i> represent	<i>read</i> represents
635	13	<i>for</i> UNDUE	<i>read</i> ABNORMAL
643		<i>after</i> line 10	<i>insert</i> Abnormal Toxicity, Test for Freedom from . . . 635
668	49	<i>for</i> Undue	<i>read</i> Abnormal
708	16	<i>for</i> undue	<i>read</i> Abnormal
710	33	<i>for</i> Undue	<i>read</i> Abnormal
711		<i>delete</i> line 1	

ADDITIONAL CORRIGENDA IN THE FIRST ISSUE
(SEPTEMBER, 1932)

<i>page line</i>			
185	30	<i>delete</i> , as directed under 'Pilula Ferri Carbonatis'	
274	6	<i>delete</i> Test for Purity. This solution satisfies the <i>test for sterility.</i>	
375	46	<i>for</i> thirty	<i>read</i> fifty
507	26	<i>for</i> ruthenium oxybromide	<i>read</i> ammoniated ruthenium hydroxychloride, $\text{Ru}_2\text{Cl}_4(\text{OH})_2, 7\text{NH}_3, 2\text{H}_2\text{O}.$

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Detection of Pasteurisation, and Detection of Raw Milk in Pasteurised Milk. M. F. Bengen. (*Z. Unters. Lebensm.*, 1933, **66**, 126-136.)—Certain parts of the albumins of milk coagulate at 63° to 65° C., *i.e.* at the temperature of pasteurisation. Addition of a definite amount of ammonium sulphate to milk yields a "limiting serum" which will contain such readily coagulable albumins if the milk treated were raw, but will be devoid of them if the milk had been previously heated to 63° to 65° C. even for a few minutes. Hence, in the former case the serum becomes turbid when carefully heated to 65° C., whereas in the latter it remains clear up to 70° C. and shows turbidity only at 71° C.

The "limiting serum" is prepared as follows: 10 grms. of finely powdered ammonium sulphate are dissolved in 50 c.c. of the milk as rapidly as possible by shaking. The serum separates immediately, and may be filtered at once through a close filter-paper, such as Schleicher and Schüll's extra hard No. 605 (12.5 cm. diameter). Two serums are thus prepared, one from the milk as received, and the other from the same milk previously heated to 63° to 65° C. for 5 minutes. The two serums are then examined together to ascertain if they become turbid at the same temperature when heated or if any "turbidity-difference" exists between them.

For this purpose two test-tubes containing the serums (5 c.c.) are suspended in a roomy beaker containing water at 65° C., which is then heated so that the temperature rises about 1° C. per minute; an accurate thermometer is essential. The tubes are examined without being removed from the bath. It is advisable to use, in a third test-tube, a standard turbid solution, which renders the determination of the turbidity point more exact and is prepared as follows: 0.3 gm. of raw potato starch is mixed with cold water, the mixture being then made up to about 50 c.c., and kept boiling gently for 10 minutes; after addition of 15 c.c. of glycerin, the boiling is continued for 10 minutes. The liquid is then quickly cooled, mixed with 25 c.c. of alcohol, and made up to 100 c.c. In stoppered vessels it keeps well. Five c.c. of this solution, covered with a layer of liquid paraffin, is heated for 10 minutes in a water-bath at 70° C., and then has the slight turbidity suitable for comparison with the heated serums.

The method described does not indicate whether the pasteurised milk has been heated for the prescribed 30 minutes, but with a number of the milks examined it gave definite indications where the results of Schardinger's aldehydo-reductase test were inconclusive.

When many samples of milk have to be examined, a preliminary sorting test may be made by placing 5-c.c. samples of the different serums (prepared as described above) in test-tubes, and immersing these for 10 minutes in a water-bath at exactly 70° C. The serums of pasteurised milk then remain clear, whilst those of milks which

have been insufficiently heated or have been subsequently mixed with raw milk become more or less turbid. When raw milk is present the degree of turbidity is fairly closely proportional to the amount of the raw milk. T. H. P.

Determination of Sulphate in Wine by the Benzidine Method. E. Lobstein and M. Ancel. (*Ann. Chim. anal.*, 1933, **15**, 389–397.)—Determinations of sulphate in a number of red and white wines as barium sulphate by the French official method gave results from 1 to 14 per cent. lower than similar determinations made after the wines were ashed. Calculated as grms. of potassium sulphate per litre of wine, the mean difference is 0.04 to 0.05, so that the permitted quantity, 2 grms. per litre (determined by the official method), is actually about 2.05 grms. per litre.

Tests made with sulphuric acid and various sulphates show that the barium sulphate and volumetric benzidine methods yield results agreeing within 1 per cent.

Two procedures for the application of the benzidine method to wines are as follows: (1) Fifty c.c. of the wine (carefully neutralised with 0.1 *N* sodium hydroxide), 5 c.c. of 0.1 *N* hydrochloric acid, and 30 c.c. of 4 per cent. benzidine hydrochloride solution (1 per cent. solution is strong enough for white wines) are mixed in a conical flask. After 20 minutes, the liquid is filtered through a small plain filter, the flask being washed out with a neutral mixture of alcohol and ether (1 : 1), and the precipitate washed with the same mixture until free from hydrochloric acid. The filter and precipitate are shaken in a 250-c.c. conical flask with 50 to 100 c.c. of strictly neutral distilled water, and the whole is titrated with 0.1 *N* sodium hydroxide in presence of phenolphthalein, with shaking after each addition of alkali. Dissociation of the benzidine sulphate is facilitated by boiling the liquid, but under these conditions an alkali solution, standardised by titration, when hot, with standard sulphuric acid, must be used. The results thus obtained differed by 1.7 per cent. at the most from those of determinations as barium sulphate after calcination of the wine. Results accurate to within 1 per cent. may be obtained as follows:

(2) Fifty c.c. of the wine are evaporated in a 250-c.c. Pyrex flask, and the residue is calcined until white. When cold, the ash is extracted with four 20-c.c. quantities of water, which are filtered into a conical flask. The liquid is boiled for some minutes with a few drops of dilute hydrochloric acid (1 : 10) to expel carbon dioxide, and is then neutralised with 0.1 *N* sodium hydroxide solution. It is then shaken with 2 drops of dilute hydrochloric acid (1 : 10) and 100 c.c. of benzidine hydrochloride solution (0.4 per cent.), and left for 20 minutes. The subsequent operations are as described under (1). T. H. P.

Distinction of Wine Vinegar from other Vinegars. A. Patzauer. (*Chem.-Zeit.*, 1933, **57**, 735.)—The method described is based on the different forms of the crystals of calcium tartrate, etc., obtained under various conditions. Two solutions are employed: (a) 20 per cent. aqueous potassium acetate solution containing 0.5 c.c. of formaldehyde solution per 100 c.c. to prevent mould-growth; (b) 0.2 gm of *l*-tartaric acid and 0.4 gm. of crystallised sodium acetate are dissolved in 20 grms. of water, and the solution treated with 0.3 c.c. of solution (a), left

overnight, and then filtered without disturbing the sediment; the filtrate is made up to 100 c.c. and treated with 0.5 c.c. of formaldehyde solution.

In making the test, 10 c.c. of the clear filtered vinegar are shaken in a test-tube with 1 c.c. of (a), 0.5 c.c. of (b) being then added, and the liquid again shaken, and left either overnight or for some hours. If the liquid remains clear and free from deposit, the vinegar contains no wine. In presence of tartaric acid, that is, if the vinegar is derived from wine, the liquid becomes turbid within a few minutes and gives a deposit, of characteristic appearance under the microscope, after some hours. Pure wine, and also vinegar to which wine has been added, show crystals of calcium tartrate or racemate; for the latter X-shaped crystals are characteristic. Poorly fermented wine may show tufts of calcium malate. If the wine has been properly and completely fermented to acetic acid, it shows only S-shaped crystals, but if such fermentation is incomplete, oblong crystals of calcium racemate are also formed.

T. H. P.

Analytical Classification of Fish Liver Oils. N. Evers and W. Smith. (*Pharm. J.*, 1933, **131**, 128-129.)—II. *Analytical results on Fish-liver Oils.*—Further details are given of analyses reported on in Part I (*ANALYST*, 1932, **57**, 735), particularly the amount of unsaponifiable matter and its iodine value, and acid phthalic esters obtained from the soluble and insoluble in petroleum spirit, the unsaponifiable matter for six *Gadidae* fish, six Elasmobranch, 2 flat fish and the monk fish.

III. *The spectrographic examination of Fish-liver Oils.*—Twenty-nine cod-liver oils were examined for vitamin A by measuring the intensity of absorption at a wave-length of $328m\mu$, and the results were compared with the "blue values" obtained by the antimony trichloride colour test, which latter are shown to be only very approximate measures of the vitamin A value of the oil ($328m\mu$ band). The correlation between blue value and intensity of absorption at $328m\mu$ for halibut-liver oils was found not so good as was believed to be the case by Haines and Drummond (*ANALYST*, 1933, **58**, 356).

D. G. H.

Determination of Chlorogenic and Caffeic Acids. W. Plücker and W. Keilholz. (*Z. Unters. Lebensm.*, 1933, **66**, 200-238.)—The results of a number of experiments show that chlorogenic and caffeic acids may be titrated potentiometrically, with quinhydrone as indicator electrode. Chlorogenic acid in aqueous solution (50 c.c.) may be determined by treatment with 30 per cent. potassium hydroxide solution (12 c.c.) for one hour at the ordinary temperature. In this way the chlorogenic acid is converted into caffeic acid, which may then be determined by acidifying with phosphoric acid, extracting with ether, and either titrating with 0.1 N sodium hydroxide solution or determining the dry residue of the extract.

A method is worked out for the determination of chlorogenic and caffeic acids in mixtures of the two with quinic acid. The caffeic acid is precipitated as the lead compound from the ethereal solution, and the chlorogenic and quinic acids as lead salts from the aqueous solution, separate electrometric titrations being afterwards carried out. The scheme has been applied to caffeine-potassium chlorogenate, which has a known chlorogenic acid-content, in order to ascertain the

factors required for calculating the results. The method gives results which are reproducible, and, with mixtures of the two acids, accurate; quinic acid does not interfere. Unreliable results were, however, obtained from an aqueous raw coffee extract, and these were traced to the presence of citric and phosphoric acids; after these acids had been removed by precipitation with barium acetate in alcoholic solution, the method proved satisfactory. In a number of roasted coffees examined, only traces of caffeic acid could be found, and raw coffee showed no dioxystyrol.

Chlorogenic acid is an unstable compound, and is decomposed by prolonged boiling of its aqueous solution. It occurs in two different forms, having the respective specific rotations, $[\alpha]_D$, -35.45° and -47.90° . T. H. P.

Chlorogenic Acid Content of Coffee. W. Hoepfner. (*Z. Unters. Lebensm.*, 1933, 66, 238-251.)—In the determination of chlorogenic acid in coffee by the lead precipitation method, the preliminary extraction of this acid by 95 per cent. alcohol is far less complete than its extraction by water. The extent to which the lead compound is precipitated varies with the experimental conditions, and the composition of the precipitate is also variable. As a result of further work on the author's colorimetric method (*ANALYST*, 1933, 100), certain details in procedure are elaborated (*cf.* also Griebel, *ANALYST*, 1933, 621). The content of chlorogenic acid in raw coffees is found to lie between 6.3 and 7.7 per cent. (on dry matter), and that in roasted coffees varies, with the degree of roasting and the origin of the coffee, from 3.2 to 4.5 per cent.; it is possible that these limits require slight extension in both directions. In the raw beans the chlorogenic acid is present as potassium-caffeine and potassium salts; the potassium salt is the first to undergo destruction during the roasting. T. H. P.

Gravimetric Determination of the Antiseptic Constituents of Hops. T. K. Walker and J. J. H. Hastings. (*J. Inst. Brewing*, 1933, 39, 509-512.)—The authors' simplified modification (*id.*, 1929, 35, 229) of Ford and Tait's gravimetric method (*id.*, 1932, 38, 351) frequently gives high values for the α -resin, owing to the slow precipitation with it of the lead salt of a non-antiseptic substance. This may be present in the hop in amounts varying from a trace to 3 per cent., and is an acidic, almost colourless, viscous liquid, which is soluble in water or methyl alcohol, but almost insoluble in ether or petroleum spirit. The following procedure (which takes $3\frac{1}{2}$ hours) is, therefore, proposed:—About 50 grms. from the centre of the bulk sample are freshly minced to a fine meal, and 10 grms. are extracted with 100 c.c. of methyl alcohol containing no acetone or water (b.pt. 64.6° C. at 760 mm.), in the apparatus described (*loc. cit.*), or by shaking, without rotation, at intervals of 3 minutes for 20 minutes in a 300-c.c. glass-stoppered bottle with an internal diameter of not more than 5 cm. Commercial grades of methyl alcohol are unsatisfactory. When the mixture has stood for 10 minutes the liquid is poured through a fluted paper, the residual meal being pressed with a glass plunger, if necessary, in order to obtain 60 c.c. of clear filtrate. Of this, exactly 50 c.c. are mixed in a separating funnel by gentle swirling with 100 c.c. of a 1 per cent. solution of sodium chloride and 50 c.c. of petroleum spirit, and the mixture is then shaken vigorously. After separation, the petroleum layer is

filtered into a 200-c.c. flask, and the residual liquid is re-extracted with three 40-c.c. portions of petroleum spirit; the last extract should be colourless. Any tarry clots which form at the beginning of these operations should be re-dissolved in methyl alcohol separately and returned to the liquor. The paper is washed, the filtrate is diluted to 200 c.c. with petroleum spirit, and exactly 50 c.c. of the extract are evaporated in a tared flask and weighed after $1\frac{1}{2}$ hours at 100°C ., when the factor 80.8 gives the percentage of total soft resin (T). Of the remaining petroleum extract, 100 c.c. are evaporated (the last 5 c.c. being removed rapidly under reduced pressure), and a solution of the residue in not more than 20 c.c. of methyl alcohol at 45 to 50°C . is precipitated at 60°C . by the addition of a 1 per cent. solution of lead acetate in methyl alcohol containing 1 c.c. of glacial acetic acid per litre, this temperature (60°C .) being maintained for 5 minutes (*cf.* Ford and Tait, *loc. cit.*). The volume of lead acetate solution to be added is determined by a trial titration of the residue from 50 c.c. of the extract. That the necessary amount has been added is shown by the formation of a distinct brown colour when a drop of the supernatant liquid (taken immediately after the precipitate has settled) is placed on one side of a filter-paper moistened on the other with a 10 per cent. solution of sodium sulphide. After 30 minutes at room temperature the mixture is filtered on a tared sintered glass crucible, and the precipitate is washed with methyl alcohol, dried for 1 hour at 100°C ., and weighed. The percentage of α -resin is given by the factor 25.45, whilst β -resin = $(T - a)$; whence the preservative value (P) = $10(a + \beta/3)$. The above factors include corrections for the effect, on the determination, of the water present in the hops, although the result gives the percentage on the weight of hops as received, and not on the bone-dry weight. Results for 50 samples of English, American and Continental (1928–1929), and old cold-stored hops showed that Ford and Tait's method gave average results for α - and β -resins, and P higher by 0.17, 0.16 and 1.9 per cent., respectively, than the new modification.

J. G.

Precipitation of Alkaloids by Tannins and the Use of Antipyrine in the Detection of Tannins. A. H. Ware and V. Smith. (*Pharm. J.*, 1933, 131, 148–149.)—Although only 6 out of 26 alkaloidal hydrochlorides gave precipitates with gallotannin, according to Fear (*ANALYST*, 1929, 54, 316), it has been found that, with adjustment of the p_{H} value or on addition of a suitable electrolyte, probably all alkaloids may be precipitated. If 2.5 c.c. of a 1 per cent. solution of gallotannin are added to 5 c.c. of a 1 per cent. solution of the alkaloidal salt, and no precipitation occurs, 5 c.c. of a 0.1 per cent. solution of sodium bicarbonate are added, when the mixture will usually have a p_{H} value of 7 to 7.5, and will form precipitates with the hydrochlorides of amylocaine, apomorphine, arecolin, diamorphine, emetine, ephedrine, cocaine, morphine, and procaine; also with benzamine lactate, homatropine hydrobromide, physostigmine sulphate, and pilocarpine nitrate. Quinine acid hydrochloride gave a slight opalescence, increased by addition of more bicarbonate. Another method by which all the foregoing alkaloids, etc., were precipitated, and, in addition, acriflavine, theobromine sodium salicylate, and theophylline sodium acetate, consists in dissolving a little of the substance in 3 c.c. of a 10 per cent. solution of sodium acid phosphate, warming, if necessary,

and adding to the cold solution 3 c.c. of a 2 per cent. solution of gallotannin, and then sufficient, but not more than 3 c.c., of a mixed phosphate solution, which contains 5 per cent. of disodium phosphate and 10 per cent. of acid sodium phosphate. The mixture is well shaken and filtered. This test can be used for the detection of alkaloids in mixtures, vegetable powders and extractives, the substance (if solid) is moistened with a strong solution of basic lead acetate, or (if a concentrated extract) it is rubbed out with powdered wood fibre, and is then extracted with a mixture of 1 part of amyl alcohol, 1 part of carbon tetrachloride and 3 parts of chloroform. After filtration the solvent is extracted with 5 c.c. of a warm solution of sodium acid phosphate, and the test completed as above. If antipyrine is used as a routine reagent for tannins, 5 c.c. of freshly prepared aqueous extractive are treated with 0.5 gm. of acid sodium phosphate, the mixture is filtered, and the filtrate poured into 5 c.c. of a 2 per cent. solution of antipyrine. If only a slight precipitate is obtained, the test is repeated with 0.01 gm. of sodium bicarbonate instead of phosphate, and if no precipitate then forms tannin is almost certainly not present. If precipitation occurs, the mixture is evaporated to expel alcohol, filtered, adjusted to the original volume, and the filtrate is tested as above. Antipyrine is not very suitable for quantitative work, as tannin may be lost during the process of washing out the sodium phosphate. D. G. H.

Chemical Tests for *Strophanthus*. E. M. Smelt. (*Pharm. J.*, 1933, 131, 150–151.)—In order to distinguish the various species of *Strophanthus* the six following tests should be applied to the residues obtained after crushing 0.25 gm. of seeds and digesting with 10 ml. of alcohol (70 per cent.) at about 60° C. for 5 minutes, filtering the cooled mixture through cotton wool, evaporating the filtrate, and removing fat from the residue by washing twice with petroleum spirit. In each case approximately 1 mgrm. of residue is mixed with the reagent and allowed to stand:—(i) One drop of 75 per cent. v/v sulphuric acid; (ii) 1 drop of test solution of ferric chloride B.P. and 1 drop of sulphuric acid; (iii) 5 ml. of hydrochloric acid containing 1 per cent. w/v of phenol, warmed to 50°–60° C.; (iv) 1 drop of phenoldisulphonic acid (B.P. 1914 formula); (v) 0.1 ml. of a 1 per cent. v/v solution of furfural dissolved in 95 per cent. alcohol and 0.5 ml. of 75 per cent. v/v sulphuric acid added; (vi) 5 ml. of hydrochloric acid containing 0.1 per cent. w/v of resorcinol, heated to 60° C. for about 5 minutes. By these tests (a) *Strophanthus Kombé* (the only species recognised in the B.P. 1932) is readily distinguished from (b) *Strophanthus Eminii* by test (i) (a) green, (b) brown turning to violet colour; (iii) (a) red-brown tinge, (b) violet colour; (v) (a) greenish-grey in 5 minutes, indigo blue in 15 minutes, and (b) deep violet; (vi) (a) red-orange, and (b) purple colours. The same tests distinguish (c) *Strophanthus gratus* and (d) *Strophanthus sarmentosus*, (i) (c) orange-pink, (d) pink in 5 minutes; (iii) (c) violet, (d) almost colourless; (v) (c) deep violet, (d) pink; (vi) (c) purple, (d) pale red-orange. The colours obtained with (e) *Strophanthus Nicholsonii* might be confused with those given by *Strophanthus Eminii*, but the former are usually decidedly paler, particularly in test (v). Characteristic colours were not obtained with (f) *Strophanthus hispidus* or with (g) *Strophanthus Courmontii*, although it should be possible to distinguish them. Test (iv) gave in all cases the same colours as test (i).

Colours obtained with test (ii) were: After 5 minutes, (a) green, (b) dark blue, green in 5 minutes, (c) pale brown, (d) brownish-pink, (e) green, (f) red-brown, and (g) yellowish-green.

D. G. H.

Relative Activity of Ergotoxine and Ergotamine, with special Reference to the Assay of Ergot Preparations. E. Lozinski, G. W. Holden and G. R. Diver. (*Pharm. J.*, 1933, 131, 137.)—Fluid extracts of ergot were assayed colorimetrically by Allport and Cocking's modification (*Quart. J. Pharm.*, 1932, 5, 341) of Smith's technique, and biologically by the Broom and Clark technique (*J. Pharm. Exp. Ther.*, 1932, 22, 59), using ergotoxine ethanesulphonate and ergotamine tartrate as standards. Ergotoxine and ergotamine were found to be practically equivalent by the colour assay, but by the biological method ergotamine possesses only 60 to 65 per cent. of the activity of ergotoxine, and experiments with the extracts confirmed these figures. It is suggested, therefore, that, in the colorimetric assay of ergot, a correction (60 per cent. of observed readings) should be introduced to compensate for the lower activity of the ergotamine.

D. G. H.

Determination of Acriflavine and Related Medicinal Dyes. A. D. Powell and G. F. Hall. (*Pharm. J.*, 1933, 131, 136–137.)—The method used for the examination of flavine dyes depends on the insolubility of the ferricyanides, which may be almost completely precipitated from aqueous solution on addition of excess of standard potassium ferricyanide solution. Two grms. of the sample are dissolved in 250 ml. of water, and *N* hydrochloric acid is added until the solution is faintly red to Congo-red paper. Five grms. of sodium acetate solution are then added, followed by 50 ml. of 0.1 *M* potassium ferricyanide solution, added with constant stirring. After 10 minutes the precipitate is filtered off, washed with three portions of 50 ml. each of water. Ten ml. of hydrochloric acid (sp.gr. 1.16), 10 grms. of sodium chloride, 1 gm. of potassium iodide, and 3 grms. of zinc sulphate in 10 ml. of water are then added to the combined filtrate and washings, with mixing after each addition. After 3 minutes the liberated iodine is titrated with 0.1 *N* sodium thiosulphate solution, the solution being allowed to stand for another 3 minutes before the final completion of the titration. A blank determination is made on 25 ml. of the ferricyanide solution (1 ml. of 0.1 *M* potassium ferricyanide solution is equivalent to 0.08883 gm. of acriflavine or 0.07788 gm. of euflavine).

D. G. H.

Determination of Free Sulphur [in Ointments, etc.]. N. L. Allport. (*Pharm. J.*, 1933, 131, 141–142.)—The method is based on Castiglioni's process of converting free sulphur into thiocyanate by treatment with potassium cyanide, the thiocyanate being titrated against silver nitrate after the addition of formaldehyde to remove the excess of potassium cyanide (*Z. anal. Chem.*, 1932, 91, 32). Fifty c.c. of a reagent made up of 40 grms. of potassium cyanide A.R., 90 c.c. of triethanolamine, and water to 1 litre, are added to a weighed amount of the material under examination, containing about 0.1 gm. of sulphur. Unless the material is an ointment with paraffin base, 1 gm. of simple ointment or soft paraffin is added and a little pumice, and the mixture is heated for 30 minutes

under a reflux condenser. After cooling, 10 c.c. of formaldehyde solution are added, the mixture is acidified with dilute nitric acid, and exactly 50 c.c. of 0.1 *N* silver nitrate solution are added. After the addition of 0.5 gm. of decolorising charcoal, if necessary (*e.g.* with Pulv. Glycrrh. Co.), the liquid is filtered through asbestos, the residue washed with water, and the filtrate titrated with 0.1 *N* ammonium thiocyanate solution (1 c.c. of *N*/10 $\text{AgNO}_3 = 0.0032$ gm. of sulphur). The value of the blank is found by mixing 50 c.c. of the reagent with 10 c.c. of formaldehyde acidified with nitric acid, and titrating. The results agreed well with those obtained by the oxidation process, and the method is a rapid one for sulphur ointments and compound liquorice powder.

D. G. H.

Colour Reaction of Bismuth. A. D. Powell. (*Pharm. J.*, 1933, 131, 150.)—Bismuth may be detected in about 10 ml. of an aqueous solution of the drug or chemical by adding 2 ml. of dilute hydrochloric acid and about 0.5 gm. of potassium iodide, mixing, and adding 5 ml. of industrial spirit or of acetone, and 5 to 10 ml. of ethyl acetate, when a red colour in the upper layer, which separates after shaking, indicates the presence of bismuth. For a quantitative test in the absence of lead, the material is extracted twice with ether, and the bismuth is re-extracted from the ethereal solution by shaking with 5 ml. of strong ammonium chloride solution, followed by two washings with 25 and 5 ml. of water made slightly acid with hydrochloric acid. The combined extracts are neutralised with ammonia, and excess (1 or 2 drops) of dilute hydrochloric acid is added. The ether is removed by warming, the volume of the cooled solution adjusted to 50 ml., and 1 ml. of a dilute solution of sodium sulphide is added. A control test with a definite amount of bismuth present is made and the colours compared. In the presence of copper or mercury the solution must be rendered alkaline, and potassium cyanide added. If the amount of bismuth is very small and traces of lead are present, the test solution should be concentrated to 1 to 5 ml., and placed in a narrow, stoppered cylinder; hydrochloric acid to give a concentration of 0.5 *N* is added, and then about 0.2 gm. of potassium iodide. After the addition of 5 drops, or less, of ethyl acetate, the mixture is shaken, and the colour of the upper layer is matched against a control. Bismuth may be rapidly determined by the first method in 25 ml. of urine. Coloured substances may be extracted from the urine with ether, and samples of precipitated substances should be acidified with hydrochloric acid, and an amount taken equivalent to the original 25 ml. of urine. The second method is suitable for samples of tissues and organs from animals that have been injected with bismuth.

D. G. H.

Determination of Thyroxine in the Thyroid Gland. N. F. Blau. (*J. Biol. Chem.*, 1933, 102, 269–278.)—A method is presented for the quantitative extraction of thyroxine from alkaline hydrolysates of thyroid substance, which depends upon the insolubility of thyroxine in an acid solution and upon the pronounced solubility of the acid salt of the product in butyl alcohol. Distribution ratios for thyroxine, diiodotyrosine and potassium iodide between butyl alcohol and an aqueous phase, acidified with sulphuric acid, were first determined at room temperature in the presence of the products of hydrolysis of muscle proteins and of the salt that would form upon addition of the acid to 2 *N* sodium hydroxide

solution; on the basis of the data obtained, the following procedure for the determination of thyroxine in thyroid substance was devised:—In a Kjeldahl flask 1.25 gm. of the dried, defatted gland is refluxed for 18 hours with 100 c.c. of 2 *N* sodium hydroxide solution, as recommended by Leland and Foster (*J. Biol. Chem.*, 1932, **95**, 165), then the alkaline hydrolysate is cooled, transferred to a 300-c.c. separating funnel, and cooled in running water to below room temperature. From 0.5 to 2.0 c.c., or more, of brom-cresol green indicator (prepared according to Kolthoff, *The Colorimetric and Potentiometric Determination of p_H* , New York, 1931, 30), are added until the solution assumes a greenish tint, and a 1 : 1 solution of sulphuric acid is run in from a burette fairly rapidly, and with vigorous shaking of the funnel, to prevent the formation of a heavy flocculent precipitate of the products of protein cleavage, until the colour just changes to yellow; about 0.2 c.c. more is added, and the volume of acid used is noted. A test drop is removed from the funnel with a glass rod and brought into contact with a small drop of bromphenol blue indicator. A p_H of 3.5 to 3.1 will usually be found. The total volume of solution in the funnel is calculated. To the Kjeldahl flask 1 or 2 drops of brom-cresol green are added, and just enough acid (2 to 5 drops) to adjust the reaction to about p_H 3. A volume of butyl alcohol, equal to that of the total volume of the acid solution to be extracted, is measured out, used in small portions to rinse the Kjeldahl flask, and then poured into the funnel until all has been added. The whole is shaken, then left aside to cool to room temperature for from 60 to 90 minutes. Next, the light straw-coloured aqueous layer is drawn off, leaving any slight amount of tar or interfacial precipitate which may be formed in the butyl alcohol, and a volume of 4 *N* sodium hydroxide solution, containing 5 per cent. anhydrous sodium carbonate, equal to that of the volume of butyl alcohol taken, is added, shaken for a few minutes, and left to stand for an hour or 90 minutes. The dark brown alkaline solution is drawn off to the last drop. The butyl alcohol remaining in the funnel is shaken with a volume of the sodium hydroxide-carbonate mixture equal to one-half the volume of butyl alcohol originally taken. After an hour or longer, it is well separated, the end of the funnel below the stop-cock is washed with distilled water, and the butyl alcohol is run into a distillation flask of suitable size. The funnel is rinsed with several small portions of butyl alcohol which are added to the flask. A few drops of concentrated sodium hydroxide are added, and the butyl alcohol is distilled off from a water-bath at a low pressure; the distillation is continued nearly to dryness. The residue is washed with distilled water and dilute sodium hydroxide into a 250-c.c. nickel crucible. The contents of the crucible are then evaporated over a sand-bath or hot plate to dryness and ashed, and the iodine is determined as in the method of Kendall (*J. Biol. Chem.*, 1915, **20**, 501).*

P. H. P.

Biochemical

Chemistry of the Lipids of Yeast. I. Composition of the Acetone-Soluble Fat. M. S. Newman and R. J. Anderson. (*J. Biol. Chem.*, 1933, **102**, 219–228.)—Fresh living yeast was extracted with alcohol and ether and a

* Thyroxine contains 65.3 per cent. of iodine.—ABSTRACTOR.

study was made of the lipids. The lipids obtained amounted to 6.02 per cent. calculated on the dried yeast. Further extraction of the partly defatted cells with alcohol containing 1 per cent. of hydrochloric acid yielded material amounting to 0.86 per cent. calculated on dry yeast. The authors were also interested in discovering whether the fat from a unicellular organism, such as yeast, contained any acids similar to tuberculo-stearic or phtioic acids found in tubercle bacilli. The alcohol-ether-soluble lipids were separated into phospho-lipids, acetone-insoluble fat and acetone-soluble fat. The acetone-soluble fat was saponified, and the following substances obtained: sterols, a mixture of saturated cyclic and bicyclic hydrocarbons ranging from $C_{19}H_{38}$ to $C_{34}H_{66}$, present as an impurity in the yeast used, glycerol and fatty acids. The saturated acids consisted of about 75 per cent. of palmitic and 25 per cent. of stearic acid, together with a trace of some acid lower than palmitic acid. The unsaturated acids, on catalytic reduction, gave a mixture of about 25 per cent. of palmitic and 75 per cent. of stearic acid. No appreciable amount of an acid higher than stearic acid was found in the acetone-insoluble fat or in the fat obtained by extraction of the yeast cells with alcohol containing 1 per cent. of hydrochloric acid, although Neville (*Biochem. J.*, 1913, 7, 341) and MacLean and Thomas (*Biochem. J.*, 1920, 14, 483; *ANALYST*, 1920, 45, 378) reported the presence of arachidic acid in yeast fat. The results obtained indicate that the lipids of yeast are very similar in composition to the fats found in ordinary plants and animals. No saturated liquid fatty acids similar to phtioic are present. No trace was found of the valeric acid referred to by Weichherz and Merlander (*Biochem. Z.*, 1931, 239, 21) and by Weiss (*Biochem. Z.*, 1932, 243, 269).

P. H. P.

Labile Sulphur in Proteins. H. Zahnd and H. T. Clarke. (*J. Biol. Chem.*, 1933, 102, 171-186).—The reproducibility of the values for labile sulphur obtainable with purified proteins entitles the method to be regarded as capable of furnishing one more analytical characteristic. It appears probable that in many proteins this value will approximate that for cystine sulphur; the case of egg albumin, however, and perhaps of others, points to the possible presence in proteins of components other than cystine or cysteine which yield lead sulphide when heated with alkaline plumbite. The following preliminary observations support this view:—On prolonged extraction of a neutral hydrolysate of egg white with butyl alcohol, over 70 per cent. of the total sulphur passes into the alcohol. Of this sulphur, about 15 per cent. is in a labile form; the balance is mainly present as methionine, and appears to include some thioglyoxaline. The labile sulphur in the butyl alcohol extract appears to exist substantially in the disulphide or sulphydryl condition. The proportion ascribable to cystine was not determined, owing to an unexplained alteration of cystine, caused by extraction with butyl alcohol, which inhibits the reaction of Sullivan. It is planned to investigate this point by means of the cuprous precipitation method recently described by Vickery and White (*J. Biol. Chem.*, 1932-3, 99, 701). The neutral aqueous solution remaining after the extraction contains 22 per cent. of the sulphur originally present. About two-thirds of this exists in labile form, but concordant determinations by the methods of Folin and Marenzi and of Sullivan show that only about a quarter

of the labile sulphur is present as disulphide, all of which is in the form of cystine. The major part of the non-extracted labile sulphur (one-tenth of the total sulphur in the hydrolysate) thus exists in some unrecognised form. The results of experiments involving extraction of hydrolysates containing free hydrochloric acid lead to similar conclusions. The acetone-insoluble fraction of the benzoylated hydrolysate of egg white is of interest. It contained only 4.7 per cent. of the original total sulphur, and one-quarter of its sulphur was of a labile variety which gave no response to the test of Folin and Marenzi, and, therefore, cannot have existed in the disulphide or sulphhydryl condition. P. H. P.

Relationship between the Antimony Trichloride Blue Value of Cod-liver Oils and that of their Unsaponifiable Fractions. F. J. Dyer. (*Pharm. J.*, 1933, 131, 129-130.)—The antimony trichloride value for 39 samples of cod-liver oil was determined on the oils themselves and on their unsaponifiable fractions, and in every case the latter value was higher than the former; the average results for the series showed that the value for the unsaponifiable fractions was 1.615 times that for the oil itself, and variations, which were found to be normal, were between 1.163 and 2.055. Calculation by approved statistical methods (Tippett, *Methods of Statistics*) shows that, by making the test on the oil itself, in 1 of every 2 samples the result will be at least 8.7 per cent. too high or 7.5 per cent. too low; in one of 3 samples it will be at least 13.2 per cent. too high or 11.2 too low; and in one out of 22 samples it will be at least 28 per cent. too high or 21.2 per cent. too low. In a given case, therefore, it will be necessary to decide whether this degree of inaccuracy is so great as to make it worth while to carry out the test on the unsaponifiable matter. D. G. H.

Concentration and Probable Chemical Nature of Vitamin G [B_2]. L. E. Booher. (*J. Biol. Chem.*, 1933, 102, 39-46.)—Previous work from the same laboratory by Page (*Dissertation, Columbia University, 1933*) has shown that a 10-fold concentrate of the vitamin G (B_2) in skim-milk powder may be prepared by a simple extraction with boiling 93 to 94 per cent. (by weight) ethyl alcohol, but that an attempt to concentrate the vitamin further by introduction of an ethyl ether precipitation procedure indicated that a separation of vitamin G factors had occurred at this step. The present study was designed to introduce only the mildest chemical operations, avoiding particularly precipitation procedures, in hope that a much greater concentration of vitamin G might be effected before a separation of factors was encountered. Experimental evidence is now presented which points to the probable identity of vitamin G and the water-soluble yellow, green-fluorescent pigment of whey. A very simple means is described for obtaining from whey powder a concentrate carrying 1000 vitamin G "units" per grm., corresponding with a 40- to 50-fold concentration of vitamin G in whey powder from which a large fraction of the lactose had been removed, or with a 2000-fold concentration of vitamin G in fresh whole milk. Yields of 1.5 grm. were obtained from 500 grms. of the whey powder. The chemical properties of this vitamin G concentrate agree well with the properties of lactochrome, in so far as knowledge of these is available. Although this vitamin G concentrate is not pure lactochrome, it is evident that

lactochrome is its major constituent. Measurement of the vitamin G value of this concentrate showed it to be active in somewhat less than 1 mgrm. doses, but indicated no separation of vitamin G into different components. The concentrate did not carry any significant amounts of vitamin B(B_1). In all cases the vitamin G values were measured under conditions which practically eliminated the influence of coprophagy, and were as satisfactory as the values obtained for other vitamins by the rat-growth method. Many of the general properties of the concentrate are similar to those reported for *ovoflavin*, described by Kuhn and his co-workers (*Ber.*, 1933, **66**, 317; 576), and believed to be one factor of the vitamin G(B_2) complex. P. H. P.

Toxicological and Forensic

“Ginger Paralysis” (Tri-ortho-cresyl Phosphate Poisoning). Kidd and Langworthy. (*Bull. Johns Hopkins Hosp.*, 1933, **52**, 39; *Brit. Med. J.*, Sept. 23, 1933, 579.)—A detailed history is given of the epidemic of peripheral motor paralysis of the legs and arms which occurred in the United States in 1930 (ANALYST, 1931, **56**, 474). After 20,000 cases had occurred, the cause of the paralysis was traced to the use of tri-ortho-cresyl phosphate as a cheap substitute for ginger extract. In almost every case there was tingling in the calves of the legs, followed by rapid paralysis of the legs with ankle-drop, and, a week later, similar effects on the arms. There were very few deaths, but partial recovery occurred only after some months, and in many cases the paralysis still appears to be permanent. Smith, Elvroe and Frazier (*U.S. Pub. Health Rep.*, 1930, **45**, 2509) have shown that the paralysis is produced only by tri-ortho-cresyl phosphate, and not by ortho-cresyl or by para- or meta-tri-cresyl phosphate. Poisoning by imitation apiol, prepared from ortho-tri-cresyl phosphate, has recently been reported from Holland, Yugoslavia, Germany and France (E. and A. Grosse, *Arch. exp. Path. u. Pharm.*, 1932, **168**, 473; Itallie, Harmsma and van Esveld, *id.*, 1932, **165**, 84). The paralytic dose is estimated at 3 to 9 c.c. of ortho-cresyl esters.

Lead Poisoning in the North-East of Scotland. L. S. P. Davidson, H. W. Fullerton, H. J. Rae and A. Henderson. (*Lancet*, 1933, **225**, 374–377.)—All authorities say that a quantity of lead greater than 0.05 part per 100,000 in drinking water is undesirable, and it will, therefore, come as a surprise to many public health authorities to learn that in 108 of the 160 houses examined the lead-content of the water supply exceeded this limit. The following table shows the lead-content of the 160 water supplies, analysed by Mr. C. Wilson under the direction of the Aberdeen City Analyst (Mr. A. B. Weir):

	Less than	0.05 to	0.1 to	0.25 to	0.5 to	1 to	Greater than
Parts per 100,000	0.05	0.1	0.25	0.5	1.0	1.5	1.5
No. of samples ..	52	38	36	22	5	5	2

In most cases where the lead-content was found to be above the accepted limits of safety a clinical and haematological investigation of the persons in such dwellings was made, together with a determination of the lead in their urines and faeces.

The following table gives the amounts of lead in 53 samples of urine and 27 of faeces:

Urines	Mgrms. per litre				Total
	Less than 0.1	0.1 to 0.2	0.2 to 0.5	Over 0.5	
Cases	4	24	23	2	53

Faeces	Mgrms per 100 grms. of dried faeces					Total
	Less than 5	5 to 10	10 to 25	25 to 50	Over 50	
Cases	2	7	11	5	2	27

The average amount of lead in the urine and faeces of 20 persons in the City of Aberdeen was 0.069 mgrm. per litre for the urine and 4.5 mgrms. per 100 grms. of dried faeces. These figures agree with those of Kehoe and Thamann (*J. Amer. Med. Assoc.*, 1929, **92**, 1418), and it is generally accepted that the upper normal limit is 0.1 mgrm. of lead per litre of urine and 5 mgrms. per 100 grms. of dried faeces. In the special cases investigated 92.6 per cent. of the faeces and 92.5 per cent. of the urines contained amounts of lead greater than normal. The urines and faeces examined were not obtained solely from persons drinking heavily contaminated water, but represented indiscriminate sampling of the whole group. The clinical examination showed that 8 persons were suffering from severe plumbism, and that 51 out of 102 had symptoms suggestive of it. In the haematological examination, punctate basophilia was found in 33 cases out of 59. Prolonged staining with Leishman's stain was found to be the most simple and satisfactory method of staining for the demonstration of punctate basophilia, although other methylene-blue stains were tried (McCord, *et al.*, *J. Amer. Chem. Soc.*, 1924, **82**, 1759; Piney, "Diseases of the Blood," London, 1932, p. 265).

The average lead-content of the water-supplies of the cases presenting symptoms that might be attributed to plumbism was only slightly higher than in cases presenting no such symptoms (0.54 as compared with 0.42 part per 100,000). The amounts of lead in the dried faeces were definitely higher (average 46.2 mgrms. per 100 grms.) in cases of heavily contaminated water (average 0.47 part per 100,000) than in cases of slightly contaminated water (average of 7.62 mgrms. per 100 grms. for water-supplies with an average of 0.20 part of lead per 100,000). The degree of absorption of the lead ingested was found to be a variable factor. Of the 28 cases whose urinary excretion of lead was less than 0.2 mgrm. per litre, the average amount of lead in the water-supplies was 0.44 part per 100,000. The cases excreting more than 0.2 mgrm. per litre of urine had water-supplies containing on an average 0.50 part per 100,000, or practically the same as the first group.

A relationship was established between the length of the lead pipe conveying the water, the plumbo-solvent property of the water, and the degree of lead contamination present. In many of the cases the lead-content of the water supply was reduced to what may be considered a safety limit by running away the water which had lain in contact with the pipe overnight. In other cases it is suggested that the plumbo-solvent action of the water should be reduced by passing it through lime chips.

Water Analysis*

Colorimetric Determination of Fluoride in Water by means of Ferric Chloride. M. D. Foster. (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 234-236.)—The method depends on the partial bleaching of ferric thiocyanate by fluoride due to the formation of a colourless complex ferric fluoride ion. The amount of bleaching is not linearly proportional to the fluoride concentration, and, moreover, sulphate, chloride, phosphate, etc., in amounts likely to occur in some waters exercise appreciable effect on the intensity of colour. The concentration of these must therefore be known, and the amount of sample solution and iron solution adjusted accordingly; the author has constructed curves connecting variation in colour with the concentration of fluoride and other ions, and reference to the original is necessary for the details (*cf.* p. 716). S. G. C.

Organic Analysis

Antimony Trichloride as a Reagent for Double Linkings. S. Sabetay. (*Compt. rend.*, 1933, 197, 557-559.)—When 1 or 2 c.c. of the Carr-Price reagent (30 grms. of antimony trichloride dissolved in chloroform to 100 c.c.) are treated with a few drops of a compound containing a double linking, a yellow, brown or red coloration, often accompanied by a coloured precipitate, appears either immediately or after a few minutes. In some cases the solution turns greenish-blue, but such colour is much less intense than that given by carotinoids. As with permanganate, the reaction with antimony chloride is not quite general for the double linking. Thus, no colour is given by styrolene, cinnamic acid, trichloroethylene, allyl alcohol, or crotonic acid, but a faint coloration is obtained with certain aldehydes. About one hundred compounds have been tested. T. H. P.

Note on the Determination of Lactic and Pyruvic Acids. W. B. Wendel. (*J. Biol. Chem.*, 1933, 102, 47-50.)—For the determination of small quantities of lactic acid in the amounts of blood obtainable from small animals the procedure of Friedemann, Cotonio and Shaffer (*J. Biol. Chem.*, 1927, 73, 335; *ANALYST*, 1927, 52, 418) has been modified, so as to reduce a variable blank originating from rubber connections of the apparatus, from reagents and from laboratory air, and also to increase the sensitiveness of the titration end-point by decreasing the volume of solution in which the bound bisulphite is titrated. The apparatus required consists of an all-glass distillation flask to which is attached a reservoir and a West indented reflux condenser. The condenser leads to a receiving tube with an efficient absorption tower. *Pure rubber tubing* is used for all rubber connections. If room air is used it should be washed with bisulphite, followed by alkali (to retain sulphur dioxide from the bisulphite). The presence of sulphur dioxide in the boiling-flask may lead to low results, due to retention of acetaldehyde. For the determination 20 to 30 c.c. of lactic acid solution, together with a pinch of talc and 5 c.c. of the acid manganous sulphate reagent (0.5 *N* sulphuric acid, *M* sodium sulphate, and 5 per cent. manganese sulphate solution) are introduced into the boiling-flask. Then 5 c.c. of 0.01 *N* potassium permanganate solution

* See also p. 717.

are placed in the reservoir, and 2 c.c. of 1 per cent. sodium bisulphite solution (2 per cent. if 1.0 mgrm. or more of lactic acid is expected) are measured into the receiving tube. Moderate suction is applied to the upper end of the absorption tower. Water is run through the condenser at such a rate as to maintain a temperature of 25 to 30° C. at the outlet during aeration. The solution in the boiling-flask is heated by means of a micro-burner to boiling point, after which the stop-cock is opened just enough to permit the permanganate solution to drip slowly through the tube below. Boiling and aerating are continued for 25 to 30 minutes, then the burner is removed and suction stopped. The absorption tower is washed twice (into the receiving tube) with 2-c.c. portions of water. The greater part of the excess bisulphite is oxidised with 0.3 to 0.4 *N* iodine solution in order to keep the volume of solution as small as possible. Final adjustment of the first end-point and determination of the bound bisulphite are carried out in the usual way with 0.01 or 0.005 *N* iodine solution. To remove excess of iodine, when the first end-point is overrun, a few drops of dilute bisulphite solution are used. A micro-burette with a detachable capillary glass tip is used for the titrations. The residue in the boiling flask is removed by suction. The recovery of lactic acid for quantities as small as 0.1 mgrm. is as accurate as when larger amounts are analysed. In the analysis of small amounts of lactate the blank must be determined by each analyst with the apparatus and all of the reagents used. Pyruvic acid is determinable (after reduction) in small amounts (0.4 to 0.04 mgrm.) by the method with the same accuracy as previously reported for larger amounts.

P. H. P.

Determination of Phenols in River Water. Nolte. (*Chem.-Ztg.*, 1933, 57, 654.)—Disadvantages of the method previously described (*id.*, 1933, 57, 546) are insensitiveness and lack of a stable comparison standard, and the following procedure is therefore recommended:—The reagent is prepared by decolorising, with sodium nitrite, 20 c.c. of a solution of 1.38 grms. of *p*-nitraniline in 310 c.c. of *N* hydrochloric acid diluted to 1 litre with water, the resulting mixture being treated with 0.25 gm. of sodium hydroxide per 100 c.c. The sample (100 c.c.) is distilled with 5 c.c. of 25 per cent. phosphoric acid until 80 c.c. of distillate are obtained, after which 20 c.c. of distilled water are added to the flask and a further 20 c.c. distilled. A mixture of 50 c.c. of distillate and 30 c.c. of *N* sodium carbonate solution is then added to the reagent, when a red colour develops which reaches maximum intensity in 10 minutes, and may be matched against a solution of 1 gm. per litre of *m*-cresol, six comparison solutions, covering the range 0.05 to 0.3 mgrm. per litre, being used. The method gives the total steam-volatile phenols in terms of *m*-cresol. If the value exceeds 1 mgrm. per litre, the colour is too deep to match, and the solution must be diluted; if less than 0.05 mgrm. per litre is present, the solution must be made alkaline and concentrated by evaporation. J. G.

Identification of Primary Phenylethyl Alcohol, as Oxalate. L. Palfray, S. Sabetay and D. Sontag. (*Ann. Chim. anal.*, 1933, 15, 338–339.)—Five drops of the sample are boiled for 2 minutes with 0.1 gm. of anhydrous oxalic acid. The resulting mixture is boiled with 1 c.c. of water, cooled, and then boiled with 2 c.c. of 95 per cent. alcohol, when neutral phenylethyl oxalate is produced. After

recrystallisation from 80 per cent. alcohol this has a m.pt. of 51 to 51.5° C., and may be used for identification purposes (*cf.* S. Sabetay and others, *ANALYST*, 1929, **54**, 615; *Compt. rend.*, 1932, **195**, 1392).
J. G.

Detection of *p*-Phenylene-diamine. C. Griebel. (*Z. Unters. Lebensm.*, 1933, **66**, 253.)—The occurrence of *p*-diamino-anisole in hair dye, now observed, renders it impossible to rely solely on the vanillin and hydrochloric acid test previously given for *p*-phenylene-diamine (*ANALYST*, 1933, 417). It thus becomes necessary to precipitate with hypochlorite and to determine the melting point of the product of the reaction. Even so, complications may arise when mixtures containing *p*-diamino-anisole are being examined, and further investigation of this question is being undertaken.
T. H. P.

Identification of Carbonyl Compounds with 2:4-Dinitrophenyl-hydrazine. J. Ferrante and A. Bloom. (*Amer. J. Pharm.*, 1933, **105**, 381–384.)—Carbonyl compounds combine with 2:4-dinitro-phenylhydrazine to form hydrazones, and may thus be identified. This substituted phenylhydrazine is more reactive and less liable to decomposition than hydrazine. Two grms. of 2:4-dinitrophenylhydrazine are dissolved in 5 c.c. of concentrated sulphuric acid, and the mixture is made up to 50 c.c. with absolute methyl alcohol. To 10 c.c. of this solution are added 15 c.c. of absolute methyl alcohol and a methyl alcohol solution of the carbonyl compound, the latter in an amount calculated to represent slightly less than the equivalent weight of the dinitrophenylhydrazine. A change in colour occurs after addition of the first few drops of carbonyl solution. The hydrazone crystallises immediately, or after a short period of standing. Some 26 dinitrohydrazones were then prepared, including furfuralacetone, m.pt. 241.0° C.; *o*-, *m*-, and *p*-methoxycyclohexanones, m.pt.s., 135°, 133.5°, 150° C.; *p*-methoxyacetophenone, m.pt. 231.8° C.; phenylpropyl-ketone, m.pt. 188° C. The percentage of nitrogen was found for all the hydrazones, and the technique of Allen (*J. Amer. Chem. Soc.*, 1930, 2956) was found the most satisfactory.
D. G. H.

Analysis of Miscellaneous Tanning Materials. Committee Report. V. J. Mlejnek. (*J. Amer. Leather Chem. Assoc.*, 1933, **27**, 382.)—*Egg-yolk*.—The Committee unanimously recommend the method outlined in "Analysis of Leather" (Wilson and Merrill) as a provisional method. *Evaporation Losses of Oils*.—Five grms. of the oil are weighed into a tannin dish and heated for 16 hours in a combined evaporator and dryer* or other oven used for drying residues in tannin analysis. The loss of weight is calculated as a percentage on the oil.
R. F. I.

Inorganic Analysis

Colorimetric Determination of Bismuth. C. Mahr. (*Z. anal. Chem.*, 1933, **94**, 161–166.)—A colorimetric method, based on production of the yellow thiourea complex $\text{Bi}(\text{CSN}_2\text{H}_4)_5(\text{NO}_3)_2\text{OH}$ in nitric acid solution, is described. Antimony, which also gives a yellow compound, is converted into complex fluoride by addition of potassium fluoride.
W. R. S.

* The temperature is that of a boiling water-oven.—ABTRACTOR.

Precipitation of Iron, Chromium, and Aluminium by means of Hexamethylenetetramine. L. Lehrmann, E. A. Kabat and H. Weisberg. (*J. Amer. Chem. Soc.*, 1933, **55**, 3509-3511.)—The authors recommend hexamethylenetetramine instead of ammonia for the separation of iron, chromium, and aluminium from manganese, zinc, nickel, and cobalt in systematic qualitative analysis. A better separation is thus effected, and no silica or alumina is introduced, as may be the case when ammonia is used. The filtrate from the sulphides, freed from hydrogen sulphide, is boiled, and the iron is oxidised with hydrogen peroxide; the boiling solution (75 c.c.) is treated with 1 grm. of ammonium nitrate and an excess of a 10 per cent. solution of the reagent, which precipitates the trivalent metals.

W. R. S.

Determination of Titanium in Steels. T. R. Cunningham. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 305-306.)—The following method is applicable to plain carbon and alloy steels, e.g. 18 : 8 chromium-nickel steel: One half to 1 grm. of the drillings is dissolved, as far as possible, in 100 c.c. of dilute sulphuric acid (10 per cent.), with heating. The liquid is cooled to about 20° C., some ashless filter paper pulp is added, followed by cold cupferron solution (6 per cent.), drop by drop, with constant stirring, until the precipitate produced assumes a reddish-brown colour (further addition of cupferron only causes more iron to be precipitated). The precipitate, which contains all of the titanium, together with a small amount of iron, is filtered off, washed 12 to 15 times with cold dilute sulphuric acid (5 per cent.), and finally, if the steel is known to contain tungsten or molybdenum, 5 times with dilute ammonia (5 per cent.). The paper and precipitate are ashed in a platinum dish, the ash is fused with sufficient potassium pyrosulphate, and the cooled melt is dissolved in 25 c.c. of dilute sulphuric acid (10 per cent.). The titanium is determined colorimetrically by means of hydrogen peroxide in the usual way. If the steel contains an appreciable amount of copper, the residue from the sulphuric acid attack of the steel is filtered off and dissolved in nitric acid; the solution obtained is made ammoniacal and boiled to precipitate any titanium present, filtered, and the washed precipitate is ashed and added to the ignited precipitate obtained in the main cupferron precipitation. If vanadium is present, it will accompany the titanium throughout the process, and must, therefore, be separated as follows before the colorimetric determination: To the ignited cupferron precipitate contained in a platinum dish are added 5 c.c. of hydrofluoric acid (48 per cent.) and 10 c.c. of perchloric acid (60 per cent.), and the acids are evaporated to a volume of 5 c.c. or less. The solution is diluted to 50 c.c., an excess of 5 c.c. of sodium hydroxide (10 per cent.) is added, and the liquid is boiled for several minutes to precipitate the titanium, and filtered. The filter and precipitate are well washed with hot water, ashed, the residue is fused with potassium pyrosulphate, and the determination of titanium is completed as before. Good results were obtained in test experiments.

S. G. C.

Detection of Barium, Strontium, and Calcium in Systematic Qualitative Analysis. J. and H. Brintzinger. (*Z. anal. Chem.*, 1933, **94**, 166-170.)—The group precipitate obtained with ammonium carbonate in the usual qualitative

scheme may represent only a fraction of the alkaline earths present, owing partly to excessive concentration of ammonium salts introduced into the solution, partly to carbonate in the ammonia and ammonium sulphide used as precipitants for the preceding group. The authors propose precipitating the concentrated filtrate from the hydrogen sulphide precipitate with sulphuric acid, after previous evaporation to small bulk. The precipitate is collected after two hours, and extracted three times with hot dilute hydrochloric acid; a drop of the filtrate is slowly evaporated on a slide, and the residue is examined under the microscope for needles of gypsum.

If calcium is present, the precipitate must be quantitatively extracted with hydrochloric acid. The residual sulphates are reduced to sulphides in a loop of platinum wire heated in a luminous flame. The product is dissolved in a few drops of strong hydrochloric acid and the solution cleared by centrifuging. One drop is tested on a slide with a drop of 30 per cent. fluorosilicic acid. Barium yields characteristic, willow-leaf shaped crystals of BaSiF_6 . The remainder of the solution is evaporated to dryness, the residue is dissolved in two drops of water, the barium is precipitated as chromate, and the solution is centrifuged. A drop of the clear solution is tested with potassium iodate, a large drop of which is allowed to diffuse slowly into the drop of solution. Strontium under these conditions yields well-developed orthorhombic, strongly double-refracting prisms.

W. R. S.

Colorimetric Determination of Fluorine. W. D. Armstrong. (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 300-302.)—The principle used is that of the bleaching action of soluble fluorides on a coloured ferric compound, in this case ferric acetylacetonate, and a novel method of operating is adopted in order to minimise the limitations inherent in this type of method due to the fluorine and the colouring reagent in the test solution competing for the iron and giving an equilibrium which is very sensitive to variations in dilution, acidity, and content of other constituents. The method requires a Duboscq colorimeter, and a light filter, such as the Bausch and Lomb 3610, must be inserted in the eyepiece, because the colours of solutions containing different proportions of ferric acetylacetonate vary from red to yellow. *Method.*—The test solution is rendered very slightly acid, carbonate, if present, having been first removed by adding 0.1 *N* hydrochloric acid, drop by drop, to the boiling test solution, containing phenolphthalein, until the indicator no longer turns pink. To each of two 25 c.c. volumetric flasks are added 1 c.c. of ferric chloride solution (0.3 mgrm. of iron per c.c.) and 1 c.c. of acetylacetonate solution (0.5 per cent. in water). To one flask is added an aliquot part of the test solution containing not more than 0.25 mgrm. of fluorine. Both flasks are made up to the 25-c.c. mark with water, and the solutions are compared in the colorimeter, the depth of the solution containing no fluorine, being set at 20 mm., and the average of twenty separate measurements of the depth of the sample solution being taken. This process is repeated with another similar aliquot part of the sample solution to which has been added 1 c.c. of a standard sodium fluoride solution (0.1 mgrm. of fluorine per c.c.), comparing

it colorimetrically, as before, with the solution containing no fluorine. The result is calculated by the aid of the formula

$$F = \frac{(X - 20)D \cdot 0.1}{Y - X}$$

where F represents the fluorine-content of the total solution in mgrm., X is the depth-reading of the unknown solution in mm., Y is the depth-reading of the unknown solution with the added 0.1 mgrm. of fluorine, and D is the ratio of the total volume of the sample solution to the volume of the aliquot part taken. The solution must be free from any substance which forms a precipitate or undissociated salt with ferric iron or fluorine. The accuracy, which the results show to be high, is not materially affected by small quantities of neutral salts, *e.g.* sodium sulphate, sodium chloride, or by dissolved silicic acid. The method is adapted to the determination of fluorine in distillates obtained in the silicon fluoride volatilisation method (*cf.* Armstrong, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 315).
S. G. C.

Microchemical

Photometric Micro-analysis of Water. C. Urbach. (*Mikrochem.*, 1931-32, 10, 483-504; 1932, 11, 37-60; 1933, 13, 31-54; 201-224.)—Constituents of drinking water are determined by colorimetric methods, but instead of the colours being compared directly with the eye, a more accurate photometric method is used. The method depends on the fact that light of various wave-lengths passing through a coloured solution is absorbed differently for different wave-lengths, and that the amount of absorption for light of a definite wave-length is proportional to the concentration and thickness of the solution, according to the Lambert-Beer law. Light of a definite wave-length was obtained by the use of a mono chromator in which white light from a lamp was passed through strongly selective light filters transmitting light of about 450 Å (45μμ). The numbers of the filters used for the various determinations were:—S75, S72, S61, S57, S53, S50, S47, S43. A table shows the mean value of wave-length transmitted by the different filters. For coloured substances, the light extinction point for different parts of the spectrum varies, but if K is taken as the extinction constant for a thickness of 1 cm. of solution and a unit concentration (such as one mole per litre), then the extinction curve that gives the values of K in relation to the wave-length is a characteristic property of the substance being examined. Variations from the Lambert-Beer law can be detected by measuring the light-extinction point, E, for a number of different concentrations of the test solution, and for light of the same wave-length ($E = 1/a \log I_0/I$, where I_0 = initial intensity, and I that through a thickness of d cm.). The value of E is directly proportional to the concentration, and K is E/c (c = concentration); if the value of K is not constant, a calibration curve must be made. When K has been found for a given solution the concentration, c , is easily found for any dilution, $c = 1/Kd \log I_0/I$. A Pulfrich photometer was used for the determinations. The coloured solution is placed in the left container and the solvent alone in the right container, in order to make a determination to compensate for the solvent and container.

1. *Determination of Nitric Acid.*—The brucine method was found to be most suitable for photometric measurement. The brucine solution contains 0.2 gm. of brucine in 10 c.c. of sulphuric acid (free from nitric acid); for each determination 10 c.c. of the test water are used, and 1 c.c. of the freshly prepared brucine solution and 20 c.c. of sulphuric acid (free from nitric acid) are added. The mixture is shaken until it turns yellow. After cooling, it is compared with a standard nitrate solution which contains 0.02 mgrm. of N_2O_5 per c.c., of which 2 to 10 c.c. are used for a determination. The measurements should be complete within an hour after cooling. The filter S43 was found to be the most suitable. Curves are given for values of the readings compared with the different variants, together with a complete table for calculation for thicknesses of solution of 5 mm. and 10 mm., with the light-filter S43. The values of N_2O_5 per litre covered by the table extend from 0.12 mgrm. to 20.47 mgrms. Before the determination any ferrous iron is oxidised to the ferric condition by means of potassium permanganate; as this would also oxidise any nitrite, the equivalent nitrate must be extracted from the final figures (*vide infra*, abstract). A number of determinations of nitrate showed a maximum error of 5 per cent.

2. *Determination of Nitrous Acid.*—The naphthol method used by Autenrieth and Funk (*Z. anal. Chem.*, 1913, **52**, 149) was found to be most suitable for photometric measurements. *Reagents.*—(i) Two grms. of pure 1, 4-sodium naphthionate ($1, 4-C_{10}H_6[NH_2]SO_2Na$) and 1 gm. of β -naphthol are mixed with 200 c.c. of water, shaken and filtered; the colourless solution will keep in the dark. (ii) Pure hydrochloric acid (sp.gr. 1.19). (iii) Ammonia (sp.gr. = 0.903). *Method.*—Ten c.c. of the water under examination are mixed with 0.5 c.c. of the naphthol reagent, and one or two drops of concentrated hydrochloric acid, then shaken, 0.5 c.c. of ammonia added, and the mixture shaken again. The red, clear liquid, is then compared in a thickness of 20 mm. in the photometer with pure water, the light filter S50 or S53 being used. Where the nitrite concentration is high, 5 c.c. of the original sample of water are used; where it is low the thickness of liquid in the photometer is increased. Calibration curves are given, and also a table, of values of readings and the corresponding concentrations of nitrite (N_2O_3) in mgrms. per litre, with the light filter S50, and a thickness of solution of 20 mm. The values given extend from 1.8 to 0.005 mgrm. of N_2O_3 per litre. A second table gives the values in the same conditions, but with filter S53.

3. *Determination of Ammonia.*—The concentration of ammonia is determined photometrically from the colour developed with Nessler's reagent. As calcium, magnesium and iron interfere, either the ammonia must first be distilled off, or the interfering salts must be removed as double salts with Rochelle salts, or precipitated with sodium carbonate. After this preliminary treatment 1 c.c. of Nessler's reagent is added to the test solution, and a portion is transferred to the photometer container, in which the mixture should not remain more than 20 minutes. The usual calibration and colour curves are given, and a calculation table for a thickness of 30 mm. with light filter S43. The values are given as mgrms. of ammonia per 101 c.c. solution, and vary from 0.4 mgrm. to 0.0011 mgrm. The error is ± 2 per cent.; and for high ammonia values ± 0.2 per cent.

4. *Determination of Phosphorus.*—The Bell and Doisy (*J. Biol. Chem.*, 1920, 44, 55) method is used, and the blue colour developed on reduction of the phosphomolybdate complex with hydroquinone is measured photometrically; the method can be used over a much wider range of concentration than the usual colorimetric method. The colour and calibration curves are given (14 diagrams). A table is also given for the extinction coefficients for various concentration of phosphorus solutions in diffused daylight, direct sunlight, and artificial light for waiting times from 2 minutes to 140 minutes; these show that the measurement should be complete in 30 minutes, and that direct sunlight and undue rise in temperature are to be avoided. When the solution under examination has been placed in the photometer cups the reading should be completed within 2 minutes. Bell and Doisy's reagents are used. For a determination, 100 c.c. of water are treated with 2 to 3 c.c. of a saturated solution of sodium acetate and dilute acetic acid, until the reaction is acid. The calcium is then precipitated by means of an excess of ammonium oxalate solution, and the precipitate is washed with hot water, concentrated to 15 c.c., transferred to a lead glass tube and treated with 6 or 8 drops of concentrated sulphuric and 1 c.c. of concentrated nitric acid, to oxidise any organic phosphorus. When oxidation is complete the precipitate is filtered off and washed with 10 to 15 c.c. of water into a 100-c.c. graduated flask, where it is treated with 5 c.c. of molybdic acid and 5 c.c. of hydroquinone solution. After 5 minutes 25 c.c. of carbonate sulphite mixture are added, the solution is diluted to 100 c.c., and mixed, and the phosphorus is determined photometrically. Tables are given for values with filter S72, and a thickness of 5 mm., S61 and a thickness of solution of 10 mm., S61 and a thickness of solution of 30 mm., and S72 and a thickness of 30 mm. The accuracy considerably exceeds that obtainable with a colorimeter.

5. *Determination of Phosphorus. (Method 2.)*—A disadvantage of the previous method (*supra*) is that the final reading must be taken within 2 minutes of filling the photometer cups, as the colour changes. The intensity was found to reach a maximum in ten minutes, and then remained constant for 20 minutes; therefore, a new series of curves and tables are given for readings taken after the solution had remained for 10 minutes in the photometer with the illumination of the lamp passing through it. A second improvement is the use of more carbonate-sulphite solution, 32 c.c. being added instead of 25 c.c. (*vide supra*); this gives a deeper coloration, and phosphorus in concentrations hitherto giving no colour gives an appreciable colour. To prevent interference by silica, the carbonate-bisulphite solution is added before the molybdic acid, instead of 5 minutes after (*vide supra*). Tables are given of readings for values of phosphorus varying from 0.9 to 0.002 mgrm. per 100 c.c. for filter S61 and a thickness of solution of 10 mm., and from 0.3 to 0.0007 mgrm. for S61 and a thickness of 30 mm.

6. *Determination of Magnesium. (Method 1.)*—The method consists in the determination of phosphorus in precipitated magnesium phosphate by the same method as above. Denis's method (*J. Biol. Chem.*, 1922, 52, 411) is used for the precipitation of the magnesium and the formation of the molybdate. For each determination 4 c.c. of the water under examination are taken in 15-c.c. Jena glass centrifuge tubes, and 1 c.c. of dilute acetic acid, 1 c.c. of saturated sodium acetate

solution, and 1 c.c. of 4 per cent. ammonium oxalate solution are added. After being mixed and standing for 30 minutes the tubes are centrifuged at 1500 R.P.M. for 3 minutes. Then 5 c.c. of the supernatant liquid is transferred to a second centrifuge tube, and 1 c.c. of 5 per cent. ammonium phosphate solution and 4 to 5 drops of concentrated ammonia (sp.gr. 0.9) are added. After standing for 10 hours, the precipitate is centrifuged and washed 3 times with 5 c.c. of dilute (1 : 2) ammonia, and then once with 5 c.c. of 75 per cent. alcohol containing 10 c.c. of ammonia per litre. Finally, the centrifuge tube is placed over a water-bath to evaporate the ammonia, and the magnesium ammonium phosphate is transferred to a 100-c.c. graduated flask by means of 5 c.c. of 0.1 *N* sulphuric acid, followed by 15 to 20 c.c. of water. Five c.c. of ammonium molybdate solution and 5 c.c. of hydroquinone solution are next added, followed, after 5 minutes, by 32 c.c. of carbonate-sulphite solution, the mixture is diluted to the mark, and the magnesium is determined as described above for phosphorus. Tables are given with filter S61 and 10 mm. and 30 mm. thickness of solution for values of magnesium from 0.676 to 0.001 mgrm.

7. *Determination of Calcium.*—This method also depends on the precipitation of the element as phosphate, and the determination of the phosphorus in the precipitate. The method of Roe and Kahn is used (*J. Biol. Chem.*, 1926, **67**, 585; 1929, **81**, 1). As magnesium interferes, an excess of sodium hydroxide must be added before the calcium is precipitated as phosphate. For a determination, 2 c.c. of the sample are mixed in a centrifuge tube with 2 c.c. of water and 1 c.c. of 0.1 *N* sulphuric acid, and the mixture is heated over a water-bath for five minutes, after which 1 c.c. of a 25 per cent. solution of sodium hydroxide is added, followed, after 5 minutes, by 1 c.c. of 5 per cent. tri-sodium phosphate solution. After standing for 1 hour the mixture is centrifuged, the supernatant liquid is withdrawn, and the centrifuge tube is inverted to drain; the precipitate is then washed with a mixture of 50 c.c. of alcohol and 10 c.c. of amyl alcohol diluted with water to 100 c.c., and rendered just alkaline to phenolphthalein with 5 per cent. sodium hydroxide solution. After centrifuging and draining, the precipitate is dissolved in 5 c.c. of 0.1 *N* sulphuric acid, the solution is transferred to a 100-c.c. graduated flask, and the phosphorus is determined as described above. Tables are given for readings given by different concentrations of calcium with light filter S61 and thicknesses of solution of 10 mm. and 30 mm. The values range from 1.6 to 0.001 mgrm. of calcium in 2 c.c. of water. Determinations agreed within 1 or 2 per cent. of the gravimetric values for a number of different spring waters.

J. W. B.

Microchemical Detection of Coumarin. M. Wagenaar. (*Pharm. Weekblad*, 1933, **70**, 1007–1011.)—Coumarin (m.pt. 67°; b.pt. 291° C.) is slightly soluble in cold water, but very soluble in warm water, alcohol, ether, acetone or chloral hydrate. It sublimes in droplets which form characteristic crystals, and this property may be used as a means of purification or identification (sensitiveness, 1 mgrm.); the sublimate may subsequently be dissolved in warm sodium hydroxide solution and re-precipitated with acetic acid (0.02 mgrm., 1 : 500), or the crystal formation (not described) may be further developed by evaporation of a solution

in acetone. The best test is to add to a crystal of the sample 1 drop of a dilute solution of iodine in potassium iodide, when rosettes of dull blue dichroic needles of coumarin periodide are formed (0.01 mgrm., 1:1000). The reaction is less sensitive if a solution of coumarin (*e.g.* in chloral hydrate) is used, and, if the precipitate appears in an amorphous form, it should be crystallised from a solution in acetone. The rôle of the iodine is considered to be similar to that encountered in the blue adsorption compounds with narceine (which also contains a lactone group), and with starch, and the looseness of the combination is demonstrated by the removal of the blue colour on addition of sodium thiosulphate solution. If the sodium salt of coumaric acid is first formed by evaporating the sample with a solution of sodium hydroxide in alcohol, sulphur-yellow prisms are produced by evaporation of this salt with a solution of thallium nitrate. Mercuric chloride combines with coumarin to form a complex double salt, which appears as masses of radiating, long, strongly anisotropic needles. It is an advantage to add a drop of Congo red solution to aid in distinguishing between the precipitate and any crystalline unprecipitated coumarin. The most sensitive result (0.01 mgrm., 1:1000) is obtained by adding very small crystals of mercuric chloride to a solution of a few small crystals of the sample in chloral hydrate. Photomicrographs are given.

J. G.

Micro-determination of Metals in Rayon. B. P. Ridge, M. Corner and H. S. Cliff. (*J. Text. Inst.*, 1933, 24, 293-308.)—The total metal content of rayon varies between 2 and 5 mgrms. per 100 grms. of dry material. The ashing of rayon with the aid of acids is condemned, and the conditions of ashing by heat are discussed. Attack of the platinum dish by reduced metal is aggravated by alkali in the ash. In the determination of copper there is some danger of loss: (*a*) by alloying with the platinum, (*b*) by volatilisation as copper carbonyl. When the platinum is stained with copper it is better to evaporate after moistening the ash with nitric acid and ignite before the evaporation after adding hydrochloric acid. Loss by volatilisation is small for viscose rayons, but for acetate rayons it may be over 10 per cent. of the copper. Copper may be determined by a gravimetric method (precipitation as cuprous thiocyanate), by a catalytic method, or by a colorimetric method using sodium diethyldithiocarbamate, any of these methods giving reliable results. The catalytic method, however, is by far the most rapid; it depends on the fact that reduction of ferric iron by sodium thiosulphate, slow under ordinary conditions, is accelerated by the presence of copper salts proportionately to their amount. Ten grms. of the rayon yarn in pellet form are ashed in a platinum dish, and the ash is dissolved in hydrochloric acid and added to 100 c.c. of ferric alum solution (5 grms. of ferric ammonium alum and 25 c.c. of 2 *N* hydrochloric acid per litre), and 1 c.c. of 2 per cent. ammonium thiocyanate solution in a tall 500-c.c. beaker immersed in a thermostat at 20° C. Twenty-five c.c. of 0.1 *N* sodium thiosulphate solution are added, the solution is stirred, and the time taken for the red colour to disappear is noted with a stop watch. The ratio T_0/T_{Cu} is found, and the amount of copper is deduced from a curve constructed from known amounts of copper determined under similar conditions. The presence of lead, nickel, chromium, and zinc has no influence on the result.

Iron may be determined in the filtrate and washings after the removal of copper as thiocyanate. They are evaporated to dryness in a glass boiling tube, the residue dissolved in *aqua regia*, evaporated to dryness, re-dissolved in 1 c.c. of constant-boiling hydrochloric acid, and diluted with a few c.c. of water. About 0.2 gm. of pure magnesium ribbon, in small pieces, is added to the solution, and the reaction allowed to proceed until reduction is complete. Two c.c. of constant-boiling hydrochloric acid and 3 drops of a 1 per cent. solution of diphenylamine in concentrated sulphuric acid are added, and 0.02 *N* potassium dichromate solution is run in from a micro-burette until a permanent blue colour is obtained.

For the determination of zinc the ashing must be carried out in a silica dish instead of platinum. The copper in the ash solution is removed as sulphide, citric acid (0.25 c.c. of a 20 per cent. solution) is added to prevent precipitation of the iron, and the solution is neutralised with ammonia and then brought to p_H 2 to 3 with formic acid. It is then saturated at 40° C. with hydrogen sulphide, the zinc sulphide is filtered off, washed, treated with acetic acid, sodium acetate and hydroxyquinoline, and heated to 90° C., and the precipitate is filtered on to a fritted Jena glass filter. After washing, the precipitate is dried to constant weight at 150 to 160° C. (353.5 grms. of this zinc compound are equivalent to 65.38 grms. of zinc).

R. F. I.

Physical Methods, Apparatus, etc.

New Fluorescence Indicators. K. A. Jensen. (*Z. anal. Chem.*, 1933, **94**, 177-179.)—The following substances were examined, their colour-change interval being determined by means of buffer solutions of known p_H value:

	p_H interval	Colour change	Intensity of fluorescence
Benzoflavine	0.3 to 1.7	Yellow to green	Strong
3, 6-Dihydroxyphthalimide	0.0 to 2.4	Blue to green	Very strong
4-Ethoxyacridone	1.2 to 3.2	Green to blue	Very strong
3, 6-Tetramethyldiaminoxanthone	1.2 to 3.4	Green to blue	Strong
β -Naphthylamine	2.8 to 4.4	Colourless to violet	Strong
α -Naphthylamine	3.4 to 4.8	Colourless to blue	Strong
β -Methylesculetin	4.0 to 6.2	Colourless to blue	Strong
Resorufin	4.4 to 6.4	Yellow to orange	Weak
3, 6-Dihydroxyxanthone	5.4 to 7.6	Colourless to blue-violet	Strong
3, 6-Dihydroxyphthalic dinitrile	5.8 to 8.2	Blue to green	Very strong
3, 6-Dihydroxyphthalimide	6 to 8	Green to yellow-green	Very strong
Coumaric acid	7.2 to 9.0	Colourless to green	Strong
Acridine orange	8.4 to 10.4	Colourless to yellow-green	Strong
Ethoxyphenylnaphthostilbazonium chloride	9 to 11	Green to colourless	Very strong

Those compounds that show a colour change in strongly acid solution, and resorufin (which only shows a slight fluorescence) are unsuitable for use as indicators; of the others, dihydroxyphthalic nitrile and dihydroxyxanthone are the most serviceable.

W. R. S.

New Electrode-Combination for Rapid Potentiometric Analysis.
W. Hiltner. (*Chem.-Ztg.*, 1933, **57**, 704.)—The electrodes (*cf. Chem. Fab.*, 1933, p. 111) are of the bimetallic type, and consist of fused silver iodide on platinum (for oxidation-reduction and precipitation reactions) or on antimony (for neutralisation reactions). The potential is determined by the concentrations of the sparingly-soluble and feebly-dissociated complex salts formed in solutions containing many common ions. Titrations of halogen, CNS' , CrO_4'' , AsO_4'' , $(\text{COO})_2''$, SO_3'' , and S'' ions may be carried out successfully, but the method is restricted for $\text{S}_2\text{O}_3''$ and CN' ions which, when present in an excess, react with silver iodide. Silver may be determined in the presence of mercury, and chromate, oxalate, phosphate, and other radicals which form insoluble silver compounds, may be titrated as in the usual precipitation reactions. For determinations (*e.g.* of iodine or copper) involving the use of sodium thiosulphate, it is preferable to prepare a silver electrode by depositing silver on platinum electrolytically, and again electrolysing this in a solution of sodium or ammonium sulphide. Further possible developments are indicated.
J. G.

Reviews

SPIRIT TABLES. SPECIFIC GRAVITY AT 80°/80° FAHR. London: H.M. Stationery Office. 1933. Price 2s. 6d.

These tables have been compiled by Mr. F. G. H. Tate, of the Government Laboratory, London, with the approval of the Government Chemist. They are issued for use in ascertaining the strength of spirits in accordance with the regulations made under Section 4 of the Finance Act, 1907.*

The figures correlate the specific gravities of aqueous solutions of ethyl alcohol with the appropriate proof strength and with the percentage by weight of alcohol, the specific gravities being those of alcoholic solutions at 80° Fahrenheit, compared with water at the same temperature. In preparing the tables Mr. Tate has made use of the data which formed the basis of the official tables showing the corresponding figures at 60° Fahrenheit, and the values for the thermal expansion of alcohol published by the U.S. Bureau of Standards.

The determination of specific gravities of liquids at 60° F. at times when a considerably higher temperature prevails in the laboratory is a tedious process, and, moreover, involves the risk of inaccuracy, so that a cordial reception for the new tables is assured. Mr. Tate is to be congratulated on having successfully accomplished his laborious task, and deserves the thanks of the large number of scientific and technical workers to whom the tables will be indispensable. A publication from the Government Laboratory is always welcome, and the present contribution bears the hall-mark of excellence that we have come to associate with this source.

GEORGE HOGAN

* See p. 695.

BENTLEY AND DRIVER'S TEXTBOOK OF PHARMACEUTICAL CHEMISTRY. 2nd Ed.
Revised by J. E. DRIVER, Ph.D., M.Sc., A.I.C. London: Oxford University
Press. 1933. Price 16s.

The second edition of this textbook has been revised by Dr. Driver, and, as it follows closely the publication of the 1932 edition of the British Pharmacopoeia, it includes practically everything in the official book of reference which is published "By Authority" entrusted to the General Medical Council. The author acknowledges this as the source of much material for his pages, and, indeed, no textbook on pharmaceutical chemistry would be complete without constant reference to the pharmacopoeial standards.

The author has managed to include in a volume of 522 closely printed pages, with 16 more for an index, all the chemistry required by students training for pharmaceutical examinations, and, because of the numberless changes, additions and alterations which have been made in the materials used in medicine during the past decade, the book should be very acceptable to post-graduate readers also, for it is, in every sense, a book of reference for pharmacists in particular, and for every chemist who handles or manufactures medicinal products.

The *chemistry* of fifty years ago was a subject that could be adequately dealt with in a comprehensive textbook, but the changes and discoveries of recent years require a wider knowledge in every direction, and the author has left nothing of these modern aspects of the subject out of his pages, although he has been able to eliminate the elementary facts which do not need repetition.

The text is arranged in four parts, dealing, respectively, with analytical methods, inorganic chemistry, organic chemistry, and appendices and analytical tables. The first section, dealing with analysis, describes the methods and instruments used for the determination of physical constants, methods of gravimetric and volumetric analysis, and discusses at length and with lucidity, hydrogen ion concentration, indicators, and, with greater detail, the subject of p_H values and their determination. This section is quite new, so far as it relates to the pages of the British Pharmacopoeia, and will be helpful to all teachers and students of pharmacy.

The section on impurities in pharmacopoeial substances deals particularly with the "official" methods of testing medicinal substances for the presence of arsenic and lead, and adds little to the information given in the "B.P." itself. The author considers the Gutzeit method inferior to the Marsh-Berzelius method, and states that the stains on the mercuric chloride paper are sensitive to light and affected by damp and by other gases, which is perfectly correct, but he does not mention the fact that papers which show no coloration after use, in daylight, may give distinct evidence of staining when viewed in ultra-violet light. In the description of the tests for lead no mention is made of the fact that citric and tartaric acids yield very unsatisfactory results if their solutions are made strongly alkaline with ammonia, before adding the other reagents.

The section dealing with inorganic materials is seemingly limited to those of pharmaceutical interest, and again, to those official in the pharmacopoeia, for otherwise one might expect to see some reference to cerium and strontium in the text, and more notice taken of lithium preparations. The pharmaceutical student

will have learnt his elementary inorganic chemistry from other textbooks; hence the author has found it possible to be brief, and in some instances almost too brief, in the description of the compounds which hold such important places in pharmacy.

The section dealing with organic chemistry and organic substances is comprehensive and includes a resumé of the "official" tests, when such are included in the pharmacopoeia. It is comprehensive because it includes organic substances of every class, from simple paraffins to complex alkaloidal derivatives, ureides, vegetable oils, essential oils, carbohydrates and glucosides. The chapter on alkaloidal assays is as complete a description of the "official" processes as can be written without quoting the Pharmacopoeia word for word, but the assay of opium or cinchona bark cannot be learnt from a book, and no textbook methods are in complete agreement with those employed by the manufacturers of quinine or morphine salts. The assay of ergot is still open to criticism, and the author avoids mention of the serious objections to any process of standardisation by methods which attempt to determine the proportion of ergotoxine in the drug. The hormones and vitamins are afforded brief notices, but they may well be relegated to a treatise on bio-chemistry, for their literature is so extensive.

A critical examination of the whole of the text shows it to be free from notable errors; the index is complete and the cross references correct and numerous. The author may be congratulated on successfully gathering so great an amount of information in correct form into the space at his disposal, and also on the readable manner in which he has presented the many and various subjects which are comprised under the title "Pharmaceutical Chemistry."

C. EDWARD SAGE

DIE PRAXIS DER QUANTITATIVEN ORGANISCHEN MIKROANALYSE. By ALFRED FRIEDRICH, Ph.D. Pp. viii + 209, with 49 Figures. Leipzig and Vienna: Franz Deuticke. 1933. Price R.M.6.

The increasing popularity of organic micro-methods is indicated by the number of new books on the subject, although inevitably the matter must contain a large proportion of that previously published in Pregl's book. Dr. Friedrich, who was a pupil of Pregl, has had fourteen years' experience of micro-methods, and he has incorporated it in this very clearly-written and handy practical book. The mechanism and use of the micro-balance are well described, and the difference between the method of weighing by swings on the micro-balance and in ordinary analytical procedure is well brought out. This point was never emphasised by Pregl in his book, with the result that many workers have been known to use the micro-balance incorrectly. The long section on the micro-combustion analysis of carbon and hydrogen may be criticised in that the unchanged Pregl method is only briefly described in four pages without diagrams, whilst the author's "simplified" method occupies 19 pages. The author criticises the Pregl method, and states that it is suitable only for series of determinations, and that when the tube is left for a long time between analyses, considerable time is required to render the tube serviceable again, and it should be refilled. This has not been the experience of the reviewer, or that of a number of other workers, who have found that after an interval without use the tube is again in order without refilling, if,

before being used, it is heated for short periods, alternately in currents of oxygen and air, for 4 to 6 hours, an operation that needs practically no attention. The author states that the objection to the Pregl filling is due to the use of the lead peroxide which is permanently in the tube; he, therefore, uses a removable filling and places the lead peroxide in two micro-boats of Jena glass, and uses them only for compounds containing nitrogen, halogen or sulphur. The oxidising filling is replaced by a platinum contact. The pressure-regulator is replaced by a more accurate apparatus for measuring the velocity and pressure of the gas. For the absorption tubes, soda-lime and calcium chloride are used, but phosphorus pentoxide and ascarite (soda-asbestos), which have been used with success by many workers, are not recommended. The new method is interesting, but, until it has been tested thoroughly in a number of laboratories and in different countries, the claims made for any advantages it may have over the Pregl method must be accepted with caution.

Other methods described in the book include the micro-Dumas determination of nitrogen, the micro-Kjeldahl determination of nitrogen, the determination of halogens and sulphur, for which the method of combustion in oxygen and the micro-Carius method (omitted by Pregl from his book) are given, the determination of phosphorus and arsenic, and of metals in salts, micro-electroanalysis, and the determination of carbonyl, methoxyl and ethoxyl methylimide, acetyl, and active hydrogen. There are separate sections on micro-volumetric analysis and on the determination of molecular weight, and, finally, a useful chapter on apparatus.

The section on methoxyl and allied determinations, of which the author has had large experience, is very well written. A simplified micro-acetyl determination is described, and there is considerable matter which has never before been published in textbook form. It is, perhaps, a pity that more of the determinations of purely biological application could not have been included, such as the Van Slyke methods of determining amino acids, in which there have been some recent improvements, and the wet method of determining carbon, which is only mentioned. Notwithstanding these omissions, however, the work is a practical book, clearly written, and of use to all engaged in quantitative organic analysis.

JANET W. BROWN

INFRA-RED PHOTOGRAPHY. By S. O. RAWLING, D.Sc., F.I.C. Pp. x+57.
With 12 Plates and 17 Diagrams. London: Blackie & Son, Ltd. 1933.
Price 3s. 6d. net.

Photography by means of infra-red rays is by no means a new discovery, for, more than fifty years ago Abney succeeded in photographing a kettle of boiling water by its own radiation. Until recently, however, the technique was so tedious and the results so uncertain that the process had but little practical value. Even Kögel, in his monograph on the use of invisible rays in criminal investigation (*ANALYST*, 1930, **55**, 422), has given only two pages of description to infra-red photography, and regrets that so little literature on the subject is available. With the discovery of the true infra-red sensitive dyes the region of photographic sensitivity has been extended much further (to about 11,000 Å), and, with the aid of the special plates and filters now available, the process has been simplified to

such an extent that everyone can investigate its possible applications to his own branch of scientific work.

In this little textbook Dr. Rawling has assumed the reader to be familiar with the ordinary photographic processes, and gives only so much of the theory of infra-red photography as is necessary to illustrate his practical descriptions. He deals with all the difficulties that are likely to occur in connection with exposure and development, including the use of the correct filters and the illumination of the dark room.

The later part of the book describes and illustrates the various applications that have been made of infra-red photography, such as the differentiation of textile and other materials (*cf.* ANALYST, 1933, 308), haze penetration and long-distance photography, clinical record photography, photomicrography in the infra-red, and the examination of documents. Like the chapters in the earlier part, these sections are essentially practical.

The book will be found a thoroughly useful introductory guide to this newly-explored field of photography, and the only criticism that suggests itself is that a bibliography of references to the scientific literature would have added greatly to its value.

EDITOR

THE EXAMINATION OF WATERS AND WATER SUPPLIES. By JOHN CLOUGH THRESH, D.Sc., M.D., D.P.H., JOHN FOSTER BEALE, M.R.C.S., L.R.C.P., D.P.H., and ERNEST VICTOR SUCKLING, M.B., B.S., D.P.H. Fourth Edition. Pp. xvii+824 (with 61 illustrations). London: J. & A. Churchill. 1933. Price 42s.

This book is a whole-hearted honest attempt to place before analysts everything that the authors think may help any other practitioner. They draw generously and without stint on the assortment, various in the extreme, of matter they have garnered, and it is a justified guess that much of this knowledge so lavishly handed on is the outcome of substantial unselfish expenditure of time and money. No other book in English (or, so far as I know, in any foreign language) comes anywhere near it for general utility. Here we have up-to-date information on aluminium, iodine, chlorination of water and sewage, sterilisation by catadyn silver treatment, chloramine treatment, excess-lime methods, use of silicates for moorland waters, of activated carbon in purification, and the chemistry and bacterioscopy of water (fresh and sea) for swimming-bath purposes, while typical mineral analyses of 700 waters of various types prove valuable in the extreme. The pages on bacteriology have been re-written, and streptococci, anaerobes and vibrios receive fuller attention than hitherto.

An excellent feature is the description of actual difficulties encountered, to bring out the significance of different features and data. The narrative and the inferences drawn not only tend to show the certainties and the limitations of analysis, but nearly always afford better perspective than would otherwise be obtainable. It may be no disadvantage, that sometimes a certain topic is so dispersed through the book that only after much waste of time can all that the authors have to say be ascertained; thus, to ascertain the relative values of fluorescein, *B. prodigiosus*, lithium chloride, salt and calcined magnesia

in tracing the flow of a water, one has to read steadily from p. 59 to p. 73. Owing to an inadequate index which, however, is an improvement on those of earlier editions, many topics appear to be omitted that really receive attention. Thus, specimen analyses of sea-water come in under "Swimming-baths," but there is no reference to them in the index.

It is in connection with sea-water that paucity of information is most obvious. Apart from three specimen analyses of sea-water used for swimming-baths (p. 684, on which no opinion is offered), there is no information on the bacteria of clean and polluted sea-waters. There is also no statement as to the rate of disappearance of coliform organisms and typhoid bacilli, which are points of great importance not only in selecting sites for sea-bathing and intakes for swimming-pools, but also as checks on the unsuitability of outfalls for town sewage (often not even strained from gross particles), and especially in approving shell-fish layings.

As long ago as 1904, Houston's work for the Commissioners on Sewage Disposal emphasised the necessity for a basis for adjudicating the purity of sea-water. Sea-water is regrettably ignored in present-day literature: one paper by Kenwood and Kay-Menzies, and another by Purvis, Macalister and Minnett, read before the Congress of 1909, seem to pass unnoticed. All that we find in popular handbooks are statements of Houston, that *B. coli* disappears from sea-water in 5 to 9 days, and that Hewlett and Nankivell put the period of disappearance at 4 days. Purvis and his collaborators showed how *B. coli* was reduced, sometimes by 90 per cent. in six hours; this is a point of great significance, in view of the samples from littorals that are being examined after a day's storage on ice.

The authors might have spared us much out-of-date matter derogatory to chemistry. It is late in the day to quote the table of Sir E. Frankland and Dr. Tidy (p. 184), where a water with an oxygen-absorbed figure of 0·10, in upland surface water (or 0·05 in "other waters") is credited as "of great organic purity." Again, a case is quoted (p. 186) in which one per cent. of a sewage effluent added to laboratory tap-water gave (in parts per 100,000):

Nitric nitrogen	1·04
Free ammonia	0·001
Albuminoid ammonia	0·002
Oxygen absorbed	0·04

The authors say "this analysis gives no indication whatever of sewage pollution." Most analysts that I know would say at once that it does suggest sewage pollution, and would add, forcibly and pungently, that they do not limit their examination to the items named. We are not restricted to specific criteria, and all of us know the frequency with which, for one reason or another, we unequivocally condemn waters showing analyses even better than this. To take a typical case: a well with walls not tight, and receiving the washings from pail-closet refuse, perhaps six months or two years after digging it into the soil, will sometimes give lower figures for these four data, but nevertheless will be condemned on several other criteria—it may be taste, blackening and smell on ignition of the solids, and the microscopy of the cream-coloured or rust-coated particles of degenerated epithelium, and the particles of carbon and iron-rust inseparably associated with human excreta.

Incidentally, in every case I have tried so far, these particles of faecal débris give a good Pettenkofer reaction for bile, when examined in the manner described by W. F. Lowe (ANALYST, 1912, 37, 450). Also, other useful tests are available in cases of doubt.

It is unjustifiable to take certain items of a certificate and say the case depends on them. The danger lies in the fact that the student or the incompetent analyst may be influenced, or indeed misled, by half-truths. It may be that in other parts of the book the misunderstanding may be neutralised or explained, but is it reasonable to ask a reader to search 700 pages to see how far any statement is modified? Every competent analyst knows the limitations of each test, and takes elaborate precautions against being misled by it.

On the subject of dejecta the authors give no indication as to how epithelium from hands is to be differentiated from epithelium from the bowel; the use of Romanowsky stains for the differentiation of cell substance and nucleus of cells is not mentioned, nor is attention directed to the significance of the finding of stone cells of fruit or particles of the bran of cereals in intimate admixture with epithelium. It is on such items that some guidance can occasionally be given with regard to the origin of the contamination. It has its pitfalls, for, in a recent instance, the reviewer expressed the opinion that epithelium was human or from poultry, owing to particles of wheat bran being entangled in it. Enquiry by the engineer showed that it was equine, and the horses were being fed with wheat as being cheaper on the spot than oats. Page 231 leaves this item of an analyst's equipment at "dead animal matter is, as a rule, more readily recognised (*i.e.* than dead vegetable matter), as destruction by maceration is rarely so complete as to obscure the origin of the débris."

Chemical analysis of water is affected by sundry matters. For example, a useful test was simultaneously made obsolete when boric acid as a food preservative was forbidden, because, in a number of cases, an opinion that there was contamination with human sewage or urine, received confirmation on finding boric acid in a well-water. Now any reports on the Jolles test for indican (ANALYST, 1921, 46, p. 103), as evidence of animal excreta, would be welcomed.

A discovery of the authors, which is too little known, is that, by rinsing out a sample bottle with weak acetic acid it is found, on numerous occasions, that lead has deposited on the glass (p. 263 of this edition).

It would be interesting to know the state of health of the consumers of a supply where 7 parts of nitric nitrogen per 100,000 were found (p. 172); 7 parts of nitric nitrogen would equal 30 grains of sodium nitrate per gallon. The authors, in basing a calculation of a medicinal dose a day (p. 94), reckon only on a consumption of 3 pints, and they say that 3 parts of nitric nitrogen per 100,000 indicate, say, 5 grains (the medicinal dose) of sodium and potassium nitrates, and that "this figure should not be exceeded." Quite a number of men drink a gallon a day, and danger from saline constituents should be based on maximum, and not on average, intake.

If repetition be permitted, may I quote and confirm the concluding sentences from a review of the Third Edition (ANALYST, 1925, 50, p. 312): "This book is a work of sheer merit. The more it is consulted, the greater is the appreciation of the whole-hearted work the authors have done"?

W. PARTRIDGE

Publications Received

BRITISH STANDARDS INSTITUTION

BRITISH STANDARD SPECIFICATIONS (1933).

- No. 496. SAMPLING AND ANALYSIS OF COKE.
- No. 502. SAMPLING OF LARGE AND RUN-OF-MINE COAL.
- No. 503. CREOSOTE FOR FUEL IN FURNACES.
- No. 506. METHYL ALCOHOL (METHANOL).
- No. 507. ETHYL ALCOHOL.
- No. 508. NORMAL BUTYL ALCOHOL (BUTANOL).
- No. 509. ACETONE.

Price 2s. each. Post free 2s. 2d. From the Publications Department, 28, Victoria Street, London, S.W.1.

REPORT ON METRIC UNITS OF VOLUME (No. 501)

The Chemical Divisional Council of the British Standards Institution has decided that in all British Standard Specifications prepared for use in the Chemical Industry in which reference to metric units of volume is made, the unit to be employed shall be the millilitre (abbreviation ml.) in preference to cubic centimetres. For example, the millilitre has been adopted as the unit in terms of which British Standard volumetric glassware shall be calibrated, and as the unit to be employed in the description of analytical methods. The decision to adopt this unit was taken after careful consideration involving a detailed study of the history of the metric units of volume and of current practice.

A similar recommendation was made by the Joint Committee for the Standardisation of Scientific Glassware in 1924, and has since been adopted in many important publications. Some journals, however, still retain the use of "c.c." The British Standards Institution consider that the general use of the millilitre in all journals is highly desirable.

It is therefore hoped that editors of scientific journals and publication committees of scientific societies will give favourable consideration to the above recommendation and, where this has not already been done, introduce the use of the millilitre into their publications at the earliest opportunity.*

The relevant facts are outlined in a Report which has just been issued by the British Standards Institution, copies of which can be obtained from their Publications Department, 28, Victoria Street, London, S.W.1, price 2s. 2d., post free.

RUBBER IN CHEMICAL ENGINEERING. By H. P. STEVENS and M. B. DONALD. Pp. 64. Issued by the Rubber Growers' Association, Inc., 2, Idol Lane, London, E.C.3.

CONTENTS.—Properties of Rubber—Linings of Rubber Sheeting—Chemical Resistance of Rubber—Rubber Paints, Cements, etc.—Chemical Engineering Uses of Rubber—Index.

The Secretary of the Association will be pleased to send a copy of the book on receipt of three half-pence for postage.

FLUORESCENCE ANALYSIS IN ULTRA-VIOLET LIGHT. By J. A. RADLEY and JULIUS GRANT. Pp. xi+219. London: Chapman & Hall. Price 15s. net.

NACHWEIS DER BIOLOGISCH WICHTIGEN KÖRPER DURCH FLUORESLENZ. By C. DHÉRE. Pp. 209. Berlin: Urban & Schwarzenberg. Price RM. 11.50.

INTRODUCTION TO PHYSICAL CHEMISTRY. Pp. vi+492. London: Longmans, Green & Co. Price 7s. 6d.

QUALITATIVE CHEMICAL ANALYSIS. By R. K. McALPINE and B. A. SOULE. Pp. x+697. London: Chapman & Hall. Price 21s. net.

* The Council of the Society of Public Analysts and other Analytical Chemists has decided that, from January, 1934, onwards, the term "ml." shall be used in THE ANALYST in place of "c.c.," whenever this can be done without appreciable error arising.—EDITOR.