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ANALYTICAL CHEMISTRY

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ANALYTICAL CHEMISTRY.

In this year's Report, absorptiometric and radiochemical methods, which were not considered in the last Report, are now reviewed. All reference to spectroscopic methods has been omitted, but will be dealt with in the next Report. Research on absorptiometric methods has been so extensive that it has only been possible to cover the inorganic applications. It is hoped that it will be possible to review organic applications in the next Report.

The most notable events of general interest to analytical chemists in this country during 1955 were the lectures, sponsored by the Society for Analytical Chemistry, and given at various centres in England, by Professor Schwarzenbach of Zürich[1] and Professor J. Heyrovský of Prague.[2] The speakers dealt in general terms with the subjects each had pioneered, complexones and polarography, and which have had such a great impact on the development of analytical chemistry in recent years.

In July a Symposium on Microchemistry was held in Vienna under the auspices of the Austrian Microchemical Society. About 600 delegates from most parts of the world were present and some 90 papers were read.[3] At the opening ceremony, the Feigl Prize was awarded to Dr. H. Weisz for his contribution to microchemistry in developing the new ring-oven technique.[4]

General

A useful paper has been published which deals with analytical balances.[5] The design and functioning of various components are discussed and methods for assessing the sharpness and fineness of knife edges and their adjustment are described. Reference is also made to balances used for special purposes. Ulbricht[6] has described a detailed mathematical investigation concerning the effect of air buoyancy on the accuracy of weighing. Corrections for buoyancy are recommended which can be calculated from curves and formulæ. Pfundt[7] has described a riderless microbalance. A mechanical device is used for adding weights from 1 mg. upwards and a projection scale gives the 0—1 mg. readings. The left-hand pan may be removed for adding small objects. Two models have been made, for maximum loads of 20 g. and 10 g. respectively. The latter balance has an automatic tare device, a separate rider for checking sensitivity, and an external sensitivity adjustment. Both models have separate beam compartments.

Corrosion tests have been carried out on brass weights coated with two different thicknesses of tin–nickel alloy, and the results have been compared with those obtained when other materials were used.[8] The weights with the

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[1] G. Schwarzenbach, *Analyst*, 1955, **80**, 713.
[2] J. Heyrovský, *ibid.*, in the press.
[3] *Mikrochimica Acta*, 1956, in the press.
[4] *Ann. Reports*, 1954, **51**, 336.
[5] D.S.I.R. (N.P.L. Notes Appl. Sci., 1954, No. 7).
[6] H. Ulbricht, *Z. analyt. Chem.*, 1955, **145**, 161.
[7] P. Pfundt, *Mikrochim. Acta*, 1954, 539.
[8] P. H. Bigg and F. H. Burch, *Brit. J. Appl. Phys.*, 1954, **5**, 382.

heavier coating (25 μ) showed the same resistance as highly polished stainless-steel weights. The stability of mass was about the same as that of austenitic stainless-steel and rhodium-plated brass weights. Weights made from 80/20 nickel–chromium showed slightly less resistance in highly corrosive atmospheres. For the fractional weights austenitic stainless-steel was the best, followed by zirconium, tantalum, aluminium, and titanium.

The factors which must be considered when preparing standards for volumetric glassware have been detailed.[9] The units of volume, standard temperature, construction and checking of apparatus, delivery procedure, drainage time, and the delivery of non-aqueous liquids are discussed.

Kawamura [10] has found that hydrogen peroxide mixed with various mineral or organic acids effects the rapid dissolution of steels and ferro-alloys which are normally resistant to attack. For example, ferro-tungsten, rapidly dissolves in hydrogen peroxide–hydrofluoric acid, and stellite and ferro-vanadium in hydrogen peroxide–oxalic acid. Rapid methods of steel analysis are discussed using this new opening-out treatment.

A new apparatus for wet oxidation with sulphuric and nitric acid has been described [11] in which the volatile products are condensed and returned to the flask. A great saving in time and reagents is claimed.

DeFord [12] has discussed the reliability of calculations based on the law of chemical equilibrium and has indicated the factors which must be considered in order to avoid serious errors.

A historical account of the development of organic elementary analysis has been given by van der Wal.[13]

The problems which arise when complexing agents are used in titrimetric analysis have been discussed.[14] From potentiometric and colorimetric studies of the reactions involved, it is concluded that, unless polydentate reagents are used, the formation of lower complexes, particularly near the end-point when the ligand concentration is low, leads to significant errors. Various methods for detecting the end-point are considered.

Kuznetsov [15] has studied the theory involved in selecting organic co-precipitants. In certain cases it was found possible to predict suitable reagents, *e.g.*, in the precipitation of zinc thiocyanate with methyl-violet, but it was necessary to select non-salt forming organic compounds empirically.

A systematic study of several metal–diethyldithiocarbamate complexes has been made by Bode.[16] He examined the spectra and the effect of pH and masking agents on the distribution between carbon tetrachloride and the aqueous phase. Several selective determinations are suggested as a result of this work.

Irving and Rossotti [17] have discussed the factors which determine the analytical usefulness of reagents, with particular reference to the effect of

[9] D.S.I.R. (N.P.L. Notes Appl. Sci., No. 6).
[10] K. Kawamura, *Jap. Analyst*, 1953, **2**, 347, 417.
[11] J. Pien, *Ann. Fals. Fraudes*, 1954, **47**, 266.
[12] D. D. DeFord, *J. Chem. Educ.*, 1954, **31**, 460.
[13] A. A. van der Wal, *Chem. Weekblad*, 1954, **50**, 829.
[14] A. E. Martell and S. Chaberek, *Analyt. Chem.*, 1954, **26**, 1692.
[15] V. I. Kuznetsov, *Zhur. analit. Khim.*, 1954, **9**, 199.
X [16] H. Bode, *Z. analyt. Chem.*, 1954, **143**, 182.
[17] H. Irving and H. S. Rossotti, *Analyst*, 1955, **80**, 245.

structural modifications on reagents of low selectivity. Since insufficient physicochemical information is available, it is concluded that sensitivity tests are the best approach to assessing the potentialities of a reagent.

Thiosemicarbazones of several aldehydes and ketones have been examined as reagents for all the common metals at various pH levels.[18] Silver, mercury, and copper formed coloured precipitates in all cases and cobalt gave red solutions. Some of the compounds were found suitable for the determination of mercury and copper.

Several substituted dithiocarbamates have been examined as analytical reagents.[19] The most interesting appears to be ammonium tetramethylenedithiocarbamate, for much smaller amounts of buffer are required to maintain the correct pH range than with the sodium compounds. This enables the total volume to be considerably reduced.

The properties and applications of the eight known reagents available for the gravimetric determination of nitrate have been reviewed by Williams.[20]

The properties of derivatives of " oxine " continue to arouse interest. Sensitivity tests on 8-hydroxy-5-nitroquinoline indicated that it should be more selective than oxine, but unsatisfactory results were obtained when quantitative experiments were carried out.[21] The behaviour of the reagent is discussed from the standpoint of its absorption spectrum and other physical characteristics.

The analytical properties of 8-hydroxy-5-, -6-, and -7-trifluoromethylquinolines have been examined and acid dissociation constants of the first two have been determined.[22] Their behaviour is similar to that of the corresponding methyl compounds, but the 7-compound does not form a precipitate with any of the ions which have been tested. It is concluded that this anomalous behaviour is due to *ortho*-effects. The 5-methyl-7-nitroso-, 2-methyl-5-nitroso-, 7-allyl-5-nitroso-, and 5-bromo-7-(2 : 3-dibromopropyl)-derivatives of 8-hydroxyquinoline have been examined as analytical reagents.[23] Some of these derivatives are more selective than oxine and the factors which may be responsible are discussed.

Reagents

Precipitants.—A new reagent, purpureocobaltic chloride, for the gravimetric determination of tungsten has been proposed by Dupuis.[24] The paratungstate is formed at pH 5·1—6·8, and the metatungstate at pH 2·0—3·1. The paratungstate gives more accurate results and can be dissolved in ammonia solution for colorimetric measurement. However, when iron is present it is necessary to precipitate the metatungstate to avoid interference. At other pH ranges other tungstates are precipitated, but are not suitable for gravimetric analysis since their composition is not always constant.

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[18] S. S. G. Sircar and S. Sathpathy, *J. Indian Chem. Soc.*, 1954, **31**, 450.
[19] H. Malissa and E. Schoffman, *Mikrochim. Acta*, 1955, 187.
[20] M. Williams, *Ind. Chemist*, 1954, **30**, 594.
[21] H. Irving, R. G. Hollingshead, and G. Harris, *Analyst*, 1955, **80**, 260.
[22] R. Belcher, A. Sykes, and J. C. Tatlow, *J.*, 1955, 376.
[23] R. G. W. Hollingshead, *Analyt. Chim. Acta*, 1955, **12**, 201; *Chem. and Ind.*, 1954, 1260; *Research*, 1955, **8**, 9.
[24] T. Dupuis, *Mikrochim. Acta*, 1955, 851.

McCune and Arquette [25] have examined hexamminocobaltic chloride as a reagent for the separation of triphosphoric and pyrophosphoric acids, but precipitation occurred at all pH ranges. With trisethylenediaminecobaltic chloride, however, only the triphosphate was precipitated at pH 3·5, whilst at pH 6·5 only pyrophosphate was precipitated. Trimetaphosphate and tetrametaphosphate are not precipitated. Unfortunately, it was not possible to precipitate triphosphate in the presence of pyrophosphate, for recoveries were incomplete and co-precipitation occurred. An examination of similar complex precipitants, however, might yield useful results and help to solve this old problem in analytical chemistry.

Arsanilic acid has been proposed as a reagent for the gravimetric determination of bismuth.[26] Only sodium, potassium, ammonium, and acetate ions are mentioned as not interfering. Chloride, phosphate, and tartrate must be absent.

Duval and Wadier [27] recommend 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione as a specific reagent for univalent mercury. The composition of the precipitate is variable, however, and it is necessary to redissolve it in nitric acid and complete the determination by one of the usual methods.

Diallyldithiocarbamidohydrazine has been examined as a reagent for the determination of nickel and copper.[28] Nickel is precipitated in the pH range 8·1—8·7, and copper at 2·5—3·5, hence it is possible to determine both metals in mixtures. The nickel complex is weighed, but that with copper is ignited to the oxide, dissolved in acid, and determined iodometrically.

Nickel and copper can be determined gravimetrically after precipitation with resorcylaldoxime.[29] Although precipitation of the metal complexes occurs at different pH ranges, separation is not possible. Many other ions do not interfere, however, and the reagent has been used successfully for the determination of copper in brass.

o- and *p*-Chlorophenoxyacetic acid and *p*-chloro-*m*-tolyloxyacetic acid have been used for the gravimetric determination of thorium.[30] Separation from cerite earths can be achieved with one precipitation, the first being the most effective of these reagents. Thorium may also be determined in the presence of small amounts of rare earths and bismuth by using benzenephosphonic acid as reagent.[31] Precipitation is quantitative at a very low pH range. The reagent is not very selective, however, and appears to have little advantage over the host of existing reagents now available.

Colorimetric.—Solochrome Brilliant Blue B (B.C. Index No. 723) has been proposed for the colorimetric determination of beryllium.[32] It is suitable for the range 0·2—1·6 μg. per ml. A method has been developed for the determination of beryllium in air.

Bromoanilic acid (3 : 6-dibromo-2 : 5-dihydroxy-*p*-benzoquinone) has been examined as a reagent for the colorimetric determination of calcium.[33]

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[25] H. W. McCune and G. J. Arquette, *Analyt. Chem.*, 1955, **27**, 401.

[26] A. Musil and R. Pietsch, *Z. analyt. Chem.*, 1955, **144**, 347.

[27] C. Duval and C. Wadier, *Compt. rend.*, 1955, **240**, 433.

[28] N. K. Dutta and K. P. S. Sarma, *Science and Culture*, 1955, **20**, 397.

[29] A. K. Mukherjee, *Analyt. Chim. Acta*, 1955, **13**, 334.

[30] N. Eswaranarayana and Bh. S. V. R. Rao, *J. Sci. Ind. Res., India*, 1954, *B*, **13**, 657.

[31] C. V. Banks and R. J. Davis, *Analyt. Chim. Acta*, 1955, **12**, 418.

[32] J. H. Wood, *Mikrochim. Acta*, 1955, 11.

[33] L. Erdey and I. Jankovits, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 245.

After addition of a known amount of the reagent the precipitate is filtered or centrifuged off and the residual colour of the solution is measured at 530 mμ in a Pulfrich photometer.

Michal and Zyka[34] have used tetraethylthiuram disulphide as a colorimetric reagent for the determination of copper. An intense yellow-brown colour is produced with an absorption maximum at 445 mμ. The method is highly selective. Mercury(II) also forms a complex and in its presence excess of reagent should be used but there is no interference since the mercury complex is colourless.

Thiobenzamide has been recommended by Gagliardi and Haas[35] as a reagent for the colorimetric determination of copper, an intense yellow colour being produced in neutral or hydrochloric acid solutions. Only metals which give colours in a hydrochloric acid medium interfere; nitrates, chlorides, acetates, tartrates, and phosphate have no effect even in a 1000-fold excess.

Copper has also been determined colorimetrically by the formation of a chloroform-soluble complex with 2-isatoxime methyl ether.[36] The method is highly selective.

Mukherjee[37] has proposed the use of ethylenediaminebis-sulphosalicylaldehyde and *p*-aminosalicylic acid as sensitive reagents for the colorimetric determination of ferric iron. The latter is the more sensitive but several ions, notably uranyl, copper, nickel, chromate, and molybdate, interfere. The reagent can be used over a wide pH range and the colour is very stable.

Thorium may be determined colorimetrically by means of the intense violet colour produced when it is treated with carmine-red.[38] Of the usual elements associated with thorium, only ferric iron interferes. A pH of 2·5 and wavelength of 560 mμ are the most suitable conditions for measurement.

R. B.

Inorganic Qualitative Analysis

The use of thioacetamide in place of hydrogen sulphide, particularly in semimicro-qualitative analysis, continues to gain favour and many papers have been published in recent years extolling the advantages which accrue from the use of this reagent. However, in a timely paper, Lehrman and Schneider[39] point out that the indiscriminate replacement of hydrogen sulphide by thioacetamide in conventional qualitative schemes can lead to difficulties which have not been considered in earlier studies of the reagent. Thus, if oxidising agents like iron(III), arsenate, or nitric acid are present, some reagent may be destroyed, leaving an insufficient concentration in solution to effect complete precipitation of the metal sulphides; the oxidation of thioacetamide gives rise to sulphate ions which favour the loss of the alkaline-earth cations. During the hydrolysis of thioacetamide, acetate ions are formed which lower the hydrogen-ion concentration of the solution by buffer action. Under these conditions, the Group IV cations may be

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[34] J. Michal and J. Zyka, *Chem. Listy*, 1954, **48**, 1043.
[35] E. Gagliardi and W. Haas, *Mikrochim. Acta*, 1954, 593.
[36] L. Divis and J. Skoda, *Chem. Listy*, 1954, **48**, 539.
[37] A. K. Mukherjee, *Analyt. Chim. Acta*, 1955, **13**, 268, 273.
[38] N. Eswaranarayana and Bh. S. V. R. Rao, *Z. analyt. Chem.*, 1955, **146**, 107.
[39] L. Lehrman and P. Schneider, *J. Chem. Educ.*, 1955, **32**, 474.

precipitated as sulphides. Then, before the Group III cations can be precipitated as hydroxides, the excess of thioacetamide must be removed in such a way that no objectionable ions (*e.g.*, sulphate) are formed in solution. Each disadvantage has been studied experimentally and a procedure has been developed to overcome them; the only unsatisfactory feature of the method is that about 25% of the zinc is precipitated along with the Group II sulphides. Of the Group IV cations, only zinc behaves in this way. The lithium hydroxide reagent recommended by Holness and Trewick for the separation of the copper and arsenic groups has been criticised by James and Woodward.[40] They claim that if the activity of the hydroxyl ion is the main consideration in the choice of a suitable reagent, then lithium hydroxide has no advantage over sodium or potassium hydroxide. This point is proved in a critical study of the factors affecting the separation, and in place of the lithium hydroxide reagent, a 0·5N-solution of potassium hydroxide is recommended. It is not necessary to have potassium nitrate present in the reagent solution if the sulphides are precipitated from hot solution with use of a low flow-rate of hydrogen sulphide; sulphides precipitated in this way do not readily form colloids. If mercury and the Group IIB cations are present together, some mercuric sulphide dissolves in the alkali, and mercury must be looked for in both sub-groups. Tin(II) must be oxidised before precipitation with hydrogen sulphide because of the low solubility of tin(II) sulphide in 0·5N-potassium hydroxide. Heath[41] describes an alternative to the conventional procedure for the separation and identification of the Group II cations. The precipitate of metal sulphides is treated with hydrochloric acid which gives an initial separation. Further sub-groups are obtained which make the identification of the elements present an easy matter.

Weisz[42] has applied his versatile ring-oven technique to a qualitative examination of the materials used in the fabrication of some Egyptian archæological specimens. By a suitable sampling procedure, sufficient metal is removed from the specimen to provide a drop of solution which can be analysed by the ring-oven methods. Bank and van der Eijk[43] confirm Weisz's results for the qualitative examination of a drop of solution by the ring-oven method. Arsenic and mercury are now included in the scheme of analysis. Verma and Paul[44] have developed a spot-test procedure for the detection of cadmium in the presence of copper, lead, and tin. This test is more effective when ring-oven techniques are used.

Smith and Shute[45] have made a critical study of the separation and identification of aluminium in the normal scheme of qualitative analysis. Difficulty was experienced in obtaining a satisfactory test for aluminium by using ammonium aurintricarboxylate ("aluminon") because of incomplete separation of the aluminium from iron and chromium. A modified scheme has thus been recommended which uses *NN*-di(hydroxyethyl)glycine ("Versene, Fe^{3+} specific") to overcome interference from iron. Highly satisfactory results are obtained.

[40] C. F. James and P. Woodward, *Analyst*, 1955, **80**, 825.
[41] P. Heath, *ibid.*, 1954, **79**, 781.
[42] H. Weisz, *J. Chem. Educ.*, 1955, **32**, 70.
[43] C. A. Bank and W. van der Eijk, *Chem. Weekblad*, 1955, **51**, 351.
[44] M. R. Verma and S. D. Paul, *Analyst*, 1955, **80**, 399.
[45] S. B. Smith and J. M. Shute, *J. Chem. Educ.*, 1955, **32**, 380.

Numerous qualitative tests have been proposed during the year. Holzbecher[46] described the fluorescence reaction of aluminium with salicylaldehyde and 2-hydroxy-1-naphthaldehyde and 18 derivatives of these compounds. With salicylidene-*o*-aminophenol, 0·005 μg. of aluminium is detectable at a limiting concentration of 1 in 10^8. Patrovsky[47] uses this reagent for the detection of gallium. The fluorescence due to aluminium is masked by addition of sodium fluoroborate. Rhodamine-B is also used for the detection of gallium;[48] conditions are obtained which make the reaction specific for as little as 0·01 μg. of Ga^{2+}. Gagliardi and Theis[49] have examined several simple monoazo-dyes derived from 1-naphthol as reagents for the detection of magnesium in alkaline solution. Benzoin is used as a fluorescent reagent for the detection of germanium;[50] the reaction is not particularly sensitive. Pribil and Michal[51] use quercetin for the identification of vanadium; the reagent is sensitive to 2 μg. of vanadium in 5 ml. of solution. Cobalt is identified in the presence of nickel[52] by means of the deep blue colour formed with a solution containing the monothiophosphate ion, PO_3S^{3-}. The test is applicable to the solution of cobalt and nickel obtained by normal group analysis. Theis[53] describes a spot test for beryllium, using Chromazurol-S, which is sensitive to 1 μg. of beryllium in 5 ml. of solution. Chloroplumbic acid[54] has been used for the direct detection of potassium in the presence of a large number of cations, including sodium and lithium; rubidium and cæsium interfere. Sodium tetraphenylboron is recommended for the detection of potassium in systematic qualitative analysis;[55] ammonium salts, which interfere, are completely removed by a suitable procedure before carrying out the test. Rush and Rogers[56] have examined the effect of the substrate (filter-paper) on two catalytic spot-tests for copper. A 10-fold variation in sensitivity is observed between 22 grades of paper, the ashless grades in general being the most sensitive. Seely[57] has used modified spot-test techniques to detect several common ions in dust particles of 10^{-10} to 10^{-15} g.

Little new work has been published in the field of qualitative anion analysis. A systematic scheme based on Feigl's separation into soluble and insoluble zinc salts has been recommended for use on the micro- and semi-micro-scales.[58] Wendlandt and Bryant[59] describe a more reliable test for carbon dioxide than the conventional one using lime-water. The reagent is a solution of sodium methoxide in methanol, which gives a voluminous white precipitate of sodium methyl carbonate with carbon dioxide. Wirth[60]

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[46] S. Holzbecher, *Coll. Czech. Chem. Comm.*, 1954, **19**, 241.
[47] V. Patrovsky, *Chem. Listy*, 1954, **48**, 537.
[48] H. Onishi, *Analyt. Chem.*, 1955, **27**, 832.
[49] E. Gagliardi and M. Theis, *Z. analyt. Chem.*, 1955, **144**, 264.
[50] N. Appala Raju and G. Gopala Rao, *Nature*, 1955, **175**, 167.
[51] R. Pribil and J. Michal, *Chem. Listy*, 1954, **48**, 621.
[52] S. K. Yasuda and J. L. Lambert, *J. Chem. Educ.*, 1954, **31**, 572.
[53] M. Theis, *Z. analyt. Chem.*, 1955, **144**, 192.
[54] W. Rodziewicz and J. Szychlinski, *Roczniki Chem.*, 1954, **28**, 657.
[55] R. F. Muraca, H. E. Collier, J. P. Bonsack, and E. S. Jacobs, *Chemist-Analyst*, 1954, **43**, 102.
[56] R. M. Rush and L. B. Rogers, *Mikrochim. Acta*, 1955, 821.
[57] B. K. Seely, *Analyt. Chem.*, 1955, **27**, 93.
[58] F. de Leo, R. Indovina, and A. Bellino, *Ann. Chim.* (*Italy*), 1954, **44**, 859.
[59] W. W. Wendlandt and J. M. Bryant, *Chemist-Analyst*, 1955, **44**, 52.
[60] C. M. P. Wirth, *ibid.*, 1954, **43**, 101.

has developed a colour test for borates using polyvinyl alcohol; the reagent is added to an acidic solution of the borate and a drop of iodine is introduced; a deep blue colour results. Feigl and Hainberger [61] have developed a spot-test for the detection of sodium dithionite, using an ethanolic solution of *p*-dinitrobenzene; in the presence of strong aqueous ammonia an immediate orange coloration is produced with 3 µg. of dithionite.

Inorganic Gravimetric Analysis

The discovery of sodium tetraphenylboron as a reliable precipitant for potassium is one of the most important advances in inorganic analysis in recent years. Titrimetric procedures are available for the evaluation of potassium tetraphenylboron but the gravimetric method is the generally preferred one. Sykes [62] has reviewed most of the important analytical uses of sodium tetraphenylboron. Sporek and Williams [63] have made a critical examination of the published procedures for the precipitation of potassium tetraphenylboron; readily filterable precipitates are obtained when the reaction mixture has a final acidity greater than 0·2N, but it is then necessary to keep the temperature at 0° to prevent decomposition of the reagent. Cluley [64] has also studied the available methods for the determination of potassium with sodium tetraphenylboron, and he recommends two methods, involving precipitation at pH 2 and pH 6·5 respectively. The procedures are applied to the determination of potassium in glasses and refractories.

The direct determination of potassium by use of fluoroboric acid is described by Manasevit,[65] who has investigated the effect of temperature, solvent, and foreign ions on the precipitation of potassium fluoroborate. High results are obtained in the presence of ammonium, barium, and sulphate ions; calcium and aluminium interfere when present together, but not singly. A 25-fold excess of sodium can be tolerated in determinations of 20—200 mg. of potassium.

Conditions for an accurate gravimetric determination of micro-amounts of sodium as antimonate in the presence of large amounts of potassium have been worked out; [66] the precipitation is effected in 25—30% ethanol.

Lithium in small amounts is determined in the presence of other alkali metals by extraction of lithium chloride with *n*-propanol.[67] The residue obtained after removal of the solvent is dissolved in a mixture of hexamine, acetone, and water, and the mixture is treated with a reagent containing potassium ferricyanide. A yellow precipitate of a complex lithium potassium hexamine ferricyanide is obtained.

Two papers of interest in the field of gravimetric analysis deal with the hygroscopic properties of precipitates [68] and the thermogravimetry of rhodium.[69] Methods have been described for the rapid determination of

[61] F. Feigl and L. Hainberger, *Mikrochim. Acta*, 1955, 105.
[62] A. Sykes, *Ind. Chem. Mfr.*, 1955, **31**, 245, 305.
[63] K. Sporek and A. F. Williams, *Analyst*, 1955, **80**, 347.
[64] H. J. Cluley, *ibid.*, p. 354.
[65] H. M. Manasevit, *Analyt. Chem.*, 1955, **27**, 81.
[66] K. S. Cheshev, *Zhur. analit. Khim.*, 1954, **9**, 239.
[67] C. F. Forster, *Analyst*, 1954, **79**, 629.
[68] H. Amano, *J. Chem. Soc. Japan*, 1954, **75**, 499.
[69] C. Duval, P. Champ, and P. Fauconnier, *Analyt. Chim. Acta*, 1955, **12**, 138.

thorium in ores,[70] the determination of chromium as $K_2Cr_4F_5,H_2O$,[71] and the determination of bismuth as the 8-hydroxyquinoline complex.[72] Japanese workers [73] have investigated numerous binary and tertiary systems in the application of quantitative procedures without preliminary separations.

Conductivity measurements have shown[74] that barium sulphate is not precipitated from aqueous solutions until a concentration product of $1{\cdot}59 \times 10^{-8}$ (about 160 times the solubility product) is reached; spontaneous formation of nuclei then occurs. The morphology of barium sulphate has been studied by means of electron microscopy.[75] Reaction temperature and concentration of reagents have a considerable effect on the form of the precipitate which is characteristic for any set of reaction conditions.

Benedetti-Pichler [76] considers that the rate of precipitation and the particle size of a precipitate may be appreciably affected by trace impurities in the reagent. His investigations on the precipitation of barium sulphate have been prompted by the work of Bogan,[77] who claims that the particle size of barium sulphate varies according to the age of the solution used as precipitant.

Two papers presented at a Symposium on the role of reaction rates in analytical chemistry are of interest. O'Rourke and Johnson [78] discuss the kinetics and mechanism in the formation of slightly soluble ionic precipitates; they consider that precipitation occurs in two stages, involving first nucleation and growth, and secondly only the growth of the precipitate. Barium sulphate is taken as experimental model in this study of the entire process of precipitation. Gordon [79] discusses slow precipitation processes from the standpoint of precipitation from homogeneous solution. This method makes it possible to study the nature and extent of coprecipitation under very favourable conditions. Methods for the precipitation of silver chloride from homogeneous solution have been used to study the coprecipitation of thallium(I) with silver chloride.[80]

Inorganic Titrimetric Analysis

Indicators.—A search of the literature failed to provide any information on the chemical nature of " methyl-purple," an acid-base indicator mentioned in last year's Report, and recommended again this year in a titrimetric procedure for phosphorus.[81] Correspondence with the manufacturers has revealed that " methyl-purple " is a trade name for an aqueous solution of methyl-red sodium salt and patent-blue dyestuff (British Colour Index No. 714) in such proportion as to give sharp colour changes in the

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[70] M. M. Tillu and V. T. Athavale, *Analyt. Chim. Acta*, 1954, **11**, 324.

[71] Sh. T. Talipov and T. I. Fedorova, *Trudy Sredneaziatskogo Gosudarst. Univ. Khim. Nauk*, 1953, **40**, 57.

[72] A. Jílek and M. Křivánek, *Chem. Zvesti*, 1953, **7**, 563.

[73] N. Unohara, *J. Chem. Soc. Japan*, 1954, **75**, 287.

[74] W. G. Cobbett and C. M. French, *Discuss. Faraday Soc.*, 1954, 113.

[75] S. Okada and S. Magari, *Analyt. Chem.*, 1955, **27**, 1481.

[76] A. A. Benedetti-Pichler, *ibid.*, p. 1505.

[77] E. J. Bogan, *ibid.*, p. 1505.

[78] J. D. O'Rourke and R. A. Johnson, *ibid.*, p. 1699.

[79] L. Gordon, *ibid.*, p. 1704.

[80] L. Gordon, J. I. Peterson, and B. P. Burtt, *ibid.*, p. 1770.

[81] D. M. Zall, E. Wagman, and N. Ingber, *ibid.*, p. 277.

range pH 4·8—5·2. The indicator is described in a U.S. patent specification.[82] Nitrazine-yellow[83] is claimed to give a much sharper end-point and much better results than methyl-orange in acid–base titrations, but no comparison is made with newer mixed and screened indicators changing over the same pH range. A two-step mixed indicator containing bromocresol-green, New Coccine (B.C.I. No. 185), and *p*-nitrophenol is recommended for the Kjeldahl titration of ammonia in boric acid.[84] The colour change is from blue (alkaline) through grey to yellow (acid), the grey end-point at pH 4·6 being very sharp and easily seen. The cerous–ceric redox system in the presence of ferroin or nitroferroin can be used as a pH indicator in the titration of weak bases;[85] the thallous–thallic system in the presence of starch and potassium iodide behaves similarly,[86] responding to transitions of pH around 3·2 and 8·2. The indicator can be used for the titration of carbonate as a mono-acid base.

Acid-violet[87] (a triphenylmethane dye) and brilliant-yellow[88] are recommended as argentimetric adsorption indicators for halides and thiocyanate. Both are not without some of the disadvantages usually associated with this type of indicator. Aniline-blue and alkali-blue have also been used as argentimetric indicators.[89]

Gibson and White[90] have used triphenylmethylarsonium chloride as indicator in redox titrations of highly coloured solutions. Triphenylmethylarsonium permanganate and dichromate are both soluble in ethylene dichloride, forming yellow solutions, and the end-points are denoted by extraction of these substances into the organic layer.

Few new indicators have been recommended for the ever-widening field of complexometry, despite the fact that the recent literature on titrimetric analysis shows an overwhelming preference for complexometric methods. Gerlach[91] uses a mixture of dimethyl-yellow (or methyl-orange) and Eriochrome Black T for titrations with E.D.T.A.; the colour change is from grey to wine-red. Taylor[92] recommends hæmatoxylin as indicator for the direct complexometric determination of aluminium. This overcomes the necessity for a back-titration procedure involving other metal solutions. Morin[93] is used as fluorescent indicator in the direct complexometric titration of gallium and indium. Catechol-violet is a useful indicator in complexometric analysis, forming coloured complexes with cations not only in alkaline but also in acidic solution. Malat, Suk, and Ryba have developed selective and accurate methods for the titrations of bismuth[94] and thorium[95] using

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[82] U.S.P. 2,416,619, 1947.

[83] W. Buss and G. Schmidt, *Lebensmitt.*, 1954, **5**, 56.

[84] I. H. Sher, *Analyt. Chem.*, 1955, **27**, 831.

[85] E. Ranke-Madsen, H. Skarbye-Nielsen, and K. Østergaard, *Acta Chem. Scand.*, 1954, **8**, 1414.

[86] E. Ranke-Madsen and T. Kjaergård, *ibid.*, 1955, **9**, 293.

[87] G. Müller and A. Detter, *Deutsch. Apoth.-Ztg.*, 1954, **94**, 1119.

[88] J. Bognàr and J. Vereskõi, *Acta Chim. Acad. Sci. Hung.*, 1954, **5**, 91.

[89] N. F. Dobrovol'skiĭ, *Soobshch. Nauk Rabot. Vsesoyuz. Khim. Obshchei im Mendeleeva*, 1953, 12.

[90] N. A. Gibson and R. A. White, *Analyt. Chim. Acta*, 1955, **12**, 115, 413.

[91] K. Gerlach, *Angew. Chem.*, 1955, **67**, 178.

[92] M. P. Taylor, *Analyst*, 1955, **80**, 153.

[93] V. Patrovsky, *Chem. Listy*, 1953, **47**, 1338.

[94] V. Suk, M. Malat, and O. Ryba, *ibid.*, 1954, **48**, 203.

[95] *Idem, Coll. Czech. Chem. Comm.*, 1954, **19**, 679.

this indicator. Nickel, cobalt, manganese, zinc, magnesium, cadmium, and copper also form coloured complexes with catechol-violet in alkaline solution, enabling these metals to be accurately determined by direct complexometric titration.[96] Flaschka and Franschitz [97] have applied the ferrocyanide–ferricyanide–3 : 3′-dimethylnaphthidine system as a general indicator in complexometry. The method is based on an earlier procedure of Brown and Hayes.[98] Musil and Theis use Chromazurol S as indicator for the direct titration of iron, aluminium, and zirconium [99, 100, 101] with E.D.T.A. Kinnunen and Merikanto [102] have used "Zincon" as a colorimetric reagent for zinc, in place of Eriochrome Black T as indicator in the direct titration of zinc with E.D.T.A. and in back-titration procedures using standard zinc solutions. A similar approach may lead to the development of other selective indicators for the complexometric determination of metals.

Standardisation.—Gàlvez Laguarta [103] recommends using saturated solutions of certain substances as analytical standards where the concentrations are accurately known from the solubility of the solute. Suitable substances for acidimetric and alkalimetric standards are calcium hydroxide, borax, boric acid, and tartaric acid. Pierson and Gantz [104] prefer to use potassium dichromate for the standardisation of titanium(III) solutions, and they carry out the titration under carbon dioxide, using conventional redox indicators. The titanium(III) solution is best prepared from the hydride, which can be obtained in a very pure state.

Van Hall and Stone [105] describe the properties of 4-aminopyridine as a standard in acidimetry. There are few bases which can be used as analytical standards and the introduction of this base is a matter of some interest. The substance behaves as a monoprotic base, dissociation constant, $1{\cdot}6 \times 10^{-5}$; its equivalent weight is thus 94·12. 4-Aminopyridine appears to satisfy most of the requirements for a primary standard: it is a stable colourless solid (m. p. 161°) which is easily purified by recrystallisation or sublimation and is non-hygroscopic. The reagent is readily synthesised and can be recovered from titration residues. Used in the standardisation of hydrochloric acid, sharp end-points are obtained with methyl-red as indicator. The relatively high equivalent weight is another desirable feature of this substance.

Smith [106] describes a convenient method for the preparation and standardisation of small quantities of perchloratoceric acid solutions in perchloric acid, thus making an important analytical reagent of very high oxidation potential readily available. The standardisation of ammonium vanadate solutions with oxalic acid is described by West and Skoog.[107]

Duval [108] has studied the thermal stability of twelve analytical standards

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[96] V. Suk, M. Malat, O. Ryba, *Coll. Czech. Chem. Comm.*, 1955, **20**, 158.
[97] H. Flaschka and W. Franschitz, *Z. analyt. Chem.*, 1955, **144**, 421.
[98] E. G. Brown and T. J. Hayes, *Analyt. Chim. Acta*, 1953, **9**, 6.
[99] A. Musil and M. Theis, *Z. analyt. Chem.*, 1955, **144**, 351.
[100] *Idem, ibid.*, p. 427.
[101] M. Theis, *ibid.*, p. 106.
[102] J. Kinnunen and B. Merikanto, *Chemist-Analyst*, 1955, **44**, 50.
[103] E. M. Gàlvez Laguarta, *Inf. Quim. Anal.*, 1954, **8**, 153.
[104] R. H. Pierson and E. St. C. Gantz, *Analyt. Chem.*, 1954, **26**, 1809.
[105] C. E. van Hall and K. G. Stone, *ibid.*, 1955, **27**, 1580.
[106] G. F. Smith, *ibid.*, p. 1142.
[107] D. M. West and D. A. Skoog, *Analyt. Chim. Acta*, 1955, **12**, 301.
[108] C. Duval, *ibid.*, 1955, **13**, 32.

by thermogravimetry; hydrated salts show large irregularities in water content, and anhydrous forms are preferred.

Methods.—Numerous procedures have been recommended for titrimetric determination of the sulphate ion. Wilson, Pearson, and Fitzgerald [109] describe improvements to the complexometric method for the determination of 1—20 mg. amounts of sulphate; after the precipitation of barium sulphate, the excess of standard barium chloride is titrated with E.D.T.A. A similar method is described by Tettweiler and Pilz [110] for the determination of 0·01—5·0 mg. of sulphur in biological material; the excess of barium is replaced by zinc on addition of a small amount of the zinc–E.D.T.A. complex and the liberated zinc ions are titrated with E.D.T.A. Belcher, Gibbons, and West [111] apply their complexometric evaluation of barium sulphate precipitates to the determination of sulphur in steel. Geyer [112] describes the titration of sulphate, using a solution of barium chloride as titrant and alizarin-red S as indicator. The procedure does not differ appreciably from that of Fritz and Kirkland,[113] who have made a much fuller study of the titration and have published a rapid titrimetric procedure for the determination of macro-amounts of sulphate. A subsequent paper by Fritz and Yamamura [114] deals with the titration of micro-amounts of sulphate; the titration is carried out in 80% ethanol, an ethanolic solution of barium perchlorate being used as titrant and "Thorin" [2-(2-hydroxy-3 : 6-disulpho-1-naphthylazo)benzenearsonic acid] as indicator. These methods are satisfactory only with pure sulphate solutions; the microtitration is used for the determination of sulphate in raw and treated water after removal of cations by ion exchange.

Much has been published during the year on complexometric methods for the determination of many metals. It is not possible to include all the published methods in this Report, but a critical selection of the more original methods is given. The literature on the analytical applications of the complexones is becoming confusing and some attempt must shortly be made to review developments since Schwarzenbach's original publications on a really critical basis.

An interesting paper [115] describes the complexometric titration of ultramicro-amounts of calcium and magnesium in 5—20 µl. of insect hæmolymph. Bond and Tucker [116] give three methods for the titration of calcium in the presence of magnesium. Harris and Sweet [117] determine cobalt with E.D.T.A., excess of reagent being titrated with zinc. In solutions containing only nickel and cobalt,[118] the sum of both metals is determined on one aliquot part and nickel only on another aliquot part after extraction of the cobalt as the α-nitroso-β-naphthol complex. Pribil [119] determines nickel in the presence of cobalt by forming the E.D.T.A. complexes of both metals;

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[109] H. N. Wilson, R. M. Pearson, and D. M. Fitzgerald, *J. Appl. Chem.*, 1954, **4**, 488.
[110] K. Tettweiler and W. Pilz, *Naturwiss.*, 1954, **41**, 332.
[111] R. Belcher, D. Gibbons, and T. S. West, *Analyst*, 1955, **80**, 751.
[112] R. Geyer, *Z. analyt. Chem.*, 1955, **146**, 174.
[113] J. S. Fritz and M. Q. Freeland, *Analyt. Chem.*, 1954, **26**, 1593.
[114] J. S. Fritz and S. S. Yamamura, *ibid.*, 1955, **27**, 1461.
[115] K. van Asperen and I. van Esch, *Nature*, 1954, **174**, 927.
[116] R. D. Bond and B. M. Tucker, *Chem. and Ind.*, 1954, 1236.
[117] W. F. Harris and T. R. Sweet, *Analyt. Chem.*, 1954, **26**, 1648.
[118] *Idem, ibid.*, p. 1649.
[119] R. Pribil, *Chem. Listy*, 1954, **48**, 825.

nickel ions are then liberated by addition of potassium cyanide to the solution. Numerous direct and indirect procedures are recommended for the titration of aluminium.[120–124] Bismuth is titrated with E.D.T.A. in the presence of thiourea; [125] the effect of numerous ions on this titration is described. An indirect procedure [126] and a method suitable for metallurgical products [127] are also described for the complexometric determination of bismuth. Other methods have been recommended for the determination of gallium,[128] magnesium in the presence of aluminium,[129] palladium,[130] zinc in aluminium alloys,[131] and zirconium.[132]

Pribil [133] has continued his studies of 1 : 2-diamino*cyclo*hexane-*NNN′N′*-tetra-acetic acid as a titrimetric reagent; iron and manganese are titrated stepwise, and copper is determined indirectly in the presence of iron, cobalt, nickel, and manganese. Pribil [134] has also described a modified iodometric method for manganese in ores and alloys, based on the titration of the manganese(III)–E.D.T.A. complex.

Methods are given for the masking of iron,[135] iron, aluminium, and manganese,[136] and lead, bismuth, and other heavy metals [137] in titrations with E.D.T.A. Collier [138] discusses the interference of phosphate in the titration of calcium and magnesium with E.D.T.A.

Among the newer and lesser-known titrants, ascorbic acid, sodium metavanadate (vanadic acid), and chloramine-B deserve some mention. Erdey and his co-workers [139] have used ascorbic acid as a reducing titrant in the determination of silver in alloys, plating baths, and spent "hypo" solutions. The neutral or slightly acid silver solution is titrated with a standard solution of ascorbic acid, Variamine Blue (4-amino-4′-methoxydiphenylamine) being used as indicator. A procedure for the determination of oxygen in water [140] depends on the oxidation of iron(II) to iron(III) hydroxide, which is then dissolved in acid, and the iron(III) titrated with ascorbic acid. Ascorbic acid as reductant and Variamine Blue as indicator have been compared with thiosulphate and starch in several iodometric titrations; [141] good results are obtained in most of the titrations examined.

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[120] M. Theis, *Z. analyt. Chem.*, 1955, **144**, 106.
[121] I. Sajò, *Magyar Kem. Folyóirat*, 1954, **60**, 268.
[122] *Idem, ibid.*, 1953, **59**, 319.
[123] H. Flaschka and H. Abdine, *Mikrochim. Acta*, 1955, 37.
[124] E. Wänninen and A. Ringbom, *Analyt. Chim. Acta*, 1955, **12**, 308.
[125] J. S. Fritz, *Analyt. Chem.*, 1954, **26**, 1978.
[126] K. Lu Cheng, *ibid.*, p. 1977.
[127] J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1954, **43**, 88.
[128] G. W. C. Milner, *Analyst*, 1955, **80**, 77.
[129] J. A. Ritchie, *ibid.*, p. 402.
[130] W. M. MacNevin and O. H. Kriege, *Analyt. Chem.*, 1955, **27**, 535.
[131] J. C. Sergeant, *Metallurgia*, 1954, **50**, 252.
[132] A. Musil and M. Theis, *Z. analyt. Chem.*, 1955, **144**, 427.
[133] R. Pribil, *Coll. Czech. Chem. Comm.*, 1955, **20**, 162.
[134] R. Pribil and J. Vulterin, *Chem. Listy*, 1954, **48**, 1132.
[135] H. Flaschka and R. Püschel, *Z. analyt. Chem.*, 1954, **143**, 330.
[136] R. Pribil, *Chem. Listy*, 1953, **47**, 1333.
[137] R. Pribil and Z. Roubal, *ibid.*, 1954, **48**, 818.
[138] R. E. Collier, *Chem. and Ind.*, 1955, 587.
[139] L. Erdey and L. Buzàs, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 195.
[140] L. Erdey and F. Szabadvery, *ibid.*, p. 325.
[141] L. Erdey, E. Bodov, and M. Papay, *ibid.*, 1955, **5**, 235.

Singh and Sood[142] have reported further on the uses of the Chloramine-B–iodine monochloride system. In strongly acidic solution, iodide, arsenite, antimonite, mercurous chloride, stannous chloride, iron(II), hydrazine, and quinol are determined by direct titration. Indirect titrations are described for hydrogen peroxide, lead and manganese dioxides, and selenium dioxide.[143]

Vanadatometry has received considerable attention during the past year and may prove useful in some titrimetric processes. The reduction of vanadium(V) to vanadium(IV) proceeds smoothly and quite rapidly in most of the recommended procedures and visual end-points with established redox indicators are sharp. In a paper published in 1947, Willard and Manalo[144] stated that the formal potential of the system, VO_3^-/VO^{2+} is +1·02 v in 1M-sulphuric acid, rising to +1·30 v in 8M-sulphuric acid. The high acid concentration necessary in most vanadatometric procedures and the almost exclusive use of *N*-phenylanthranilic acid as indicator may thus be explained.

Molybdenum is determined by reduction to molybdenum(IV) in a bismuth reductor;[145] the reduced solution is titrated with a solution of ammonium metavanadate, *N*-phenylanthranilic acid being used as indicator. Rao, Murty, and Gopala Rao[146] find that oxalic acid catalyses the indicator reaction in the titration of uranium(IV) with vanadate solution; diphenylbenzidine or *N*-phenylanthranilic acid may be used as indicators. Hypophosphite and phosphite are both oxidised by an excess of vanadic acid in the presence of silver sulphate.[147] The excess of vanadic acid is titrated with standard iron(II) and *N*-phenylanthranilic acid as indicator. The oxidation of thiosulphate to tetrathionate and to sulphate by vanadic acid has been re-examined and suitable procedures for the titration of thiosulphate have been developed.[148] Singh and Singh titrate numerous substances directly[149] and indirectly[150] with vanadic acid in strongly acidic solutions, using iodine monochloride as indicator. These procedures are almost identical with those using Chloramine-B as titrant, described by Singh and Sood.[142] The vanadatometric determination of copper, zinc, cobalt, and mercury after precipitation of the metals as complex thiocyanates is described; lead iodide can also be titrated.

The direct titrimetric determination of carbon dioxide is described by Blom and Edelhausen.[151] This important method involves the absorption of the gas in pyridine or acetone and the titration of the solution with standard sodium methoxide in methanol, thymol-blue being the indicator. The method is applied to the determination of carbon dioxide in air and in gaseous products obtained by combustion of micro- and semimicro-amounts of organic compounds.

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[142] B. Singh and K. C. Sood, *Analyt. Chim. Acta*, 1954, **11**, 313.

[143] *Idem, ibid.*, p. 317.

[144] H. H. Willard and G. D. Manalo, *Ind. Eng. Chem. Anal.*, 1947, **19**, 462.

[145] E. V. Ankudimova, *Trudy Komissii analit. Khim. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1954, **5**, 197.

[146] V. P. Rao, B. V. S. R. Murty, and G. Gopala Rao, *Z. analyt. Chem.*, 1955, **147**, 161.

[147] G. Gopala Rao and H. S. Gowda, *ibid.*, 1955, **146**, 167.

[148] H. S. Gowda, K. B. Rao, and G. Gopala Rao, *Analyt. Chim. Acta*, 1955, **12**, 504.

[149] B. Singh and S. Singh, *ibid.*, 1954, **10**, 408; 1954, **11**, 412.

[150] *Idem, ibid.*, 1955, **13**, 405.

[151] L. Blom and L. Edelhausen, *ibid.*, p. 120.

A simple and elegant method is described by Flaschka[152] for the titrimetric evaluation of potassium tetraphenylboron. The precipitate is dissolved in acetone containing acetic anhydride, and the solution is titrated with standard perchloric acid in glacial acetic acid, crystal-violet being the indicator.

An interesting titrimetric procedure has been developed for the determination of hypophosphite in the presence of phosphite.[153] Cerium(IV) oxidises both substances quantitatively in boiling solution after 15 minutes, but at 60°, only hypophosphite is oxidised after 30 minutes. The method is accurate and precise.

W. I. S.

Classical Organic Analysis

The development of rapid methods of ultimate and functional group analysis has been reviewed,[154] and the various methods are compared. The effect of saving time by proper organisation of the laboratory and the use of riderless damped balances and of calculating machines is also discussed.

An alternative tube packing has been recommended for the determination of carbon and hydrogen to avoid radio-active cross-contamination between consecutive samples of ^{14}C-labelled compounds.[155] This consists of 7 cm. of platinum gauze, 11 cm. of granular quartz (both kept at 900—950°), 4 cm. of manganese dioxide mounted on platinised asbestos, and 3 cm. of silver-wool heated at 175°.

It has been found that low carbon values are obtained with certain sugar phosphates unless the boat is heated with the full blast of the flame.[156] This causes rapid deterioration of the combustion tube. If, however, the sample is covered with tungstic oxide, decomposition proceeds normally. Some glazing occurs at the junction of the tube with the long furnace because of attack by volatile phosphorus compounds, but this effect can be reduced by placing a boat containing tungstic oxide at this point.

Wilzbach and Sykes[157] have described a procedure for the determination of isotopic carbon in which the sample is heated with copper oxide in a sealed tube and the carbon dioxide is isolated by fractional condensation *in vacuo*. The results agree well with those obtained by less simple methods.

The rapid high-temperature method[158] for determination of carbon and hydrogen in coal has been subjected to further examination by independent workers.[159, 160] It is concluded that the method is more rapid and accurate than the Liebig method.

Ammonium sulphamate has been recommended as a substitute for lead dioxide for the absorption of nitrogen oxides.[161] More than 100 analyses can be carried out with one filling. It is not stated, however, if this reagent

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[152] H. Flaschka, *Chemist-Analyst*, 1955, **44**, 60.
[153] D. N. Bernhardt, *Analyt. Chem.*, 1954, **26**, 1798.
[154] W. Schöniger, *Angew. Chem.*, 1955, **67**, 261.
[155] J. D. Gabourel, M. J. Baker, and C. W. Koch, *Analyt. Chem.*, 1955, **27**, 795.
[156] R. Belcher, J. E. Fildes, and A. J. Nutten, *Analyt. Chim. Acta*, 1955, **13**, 431.
[157] K. E. Wilzbach and W. Y. Sykes, *Science*, 1954, **120**, 494.
[158] R. Belcher and C. E. Spooner, *Fuel*, 1941, **20**, 130.
[159] R. A. Mott and H. C. Wilkinson, *ibid.*, 1955, **34**, 169.
[160] L. J. Edgcombe, *ibid.*, p. 185.
[161] A. S. Hussey, J. H. Sorensen, and D. D. DeFord, *Analyt. Chem.*, 1955, **27**, 280.

has any advantage over other alternatives to lead dioxide reviewed in the last Report.

Sources of error in the method for the direct determination of oxygen have been investigated.[162] The quartz of the combustion tube and the carbon black must be of good quality and the temperature of the carbon must be kept constant. A simple method of purifying carbon black is proposed.

A modified method for the direct determination of oxygen has been described [163] based on the Oita–Conway method. By incorporating the fillings in one tube only one furnace is required. This method appears to be a distinct advance over the previous rather cumbersome assemblies which have been described.

A study has been made of the reaction of copper oxide with carbon dioxide in the Dumas method.[164] It is claimed that a significant amount of oxygen is formed under the usual conditions of the determination and is carried over into the azotometer. The effect is overcome by modifying both the packing of the tube and the heating arrangements.

A submicro-Kjeldahl method has been developed for amounts of nitrogen of the order of 30 μg.[165] After distillation of ammonia a colorimetric method is applied using ninhydrin as reagent.

The factors influencing sealed-tube decomposition have been studied by Kirk and his co-workers.[166] When the temperature exceeds 500° ammonium hydrogen sulphate is decomposed, yielding elementary nitrogen, and also ammonia is oxidised by sulphur trioxide or oxygen. The amount of sulphuric acid and the time of digestion may also have an influence on loss of ammonia. When a little water is added, the stability of ammonia in sulphuric acid is markedly increased. Most organic compounds are decomposed completely during 30 minutes' digestion.

Baker [167] has shown that compounds which normally do not respond to sealed-tube digestion (*e.g.*, nitro-compounds) can be analysed by mixing them with 50 mg. of glucose or *o*-mercaptobenzoic acid. A digestion temperature of 420—440° for about 45 minutes is recommended.

For microgram amounts of nitrogen, Dixon [168] recommends sodium hypobromite–sodium thiosulphate titration after digestion and distillation in the usual way, owing to the more favourable equivalent which is obtained.

A new method has been described [169] in which the compound is decomposed by heating with iodic and phosphoric acids. Nitrogen is then measured in an azotometer. However, many types of compound, particularly heterocyclic compounds, yielded poor results and the general accuracy was inferior to that of the Kjeldahl or the Dumas method.

Mikl and Pech [170] have extended a method developed some few years ago for the rapid determination of chlorine, to the determination of sulphur.

[162] L. J. Moelants and W. Wesenbeck, *Mikrochim. Acta*, 1954, 738.

[163] F. H. Oliver, *Analyst*, 1955, **80**, 593.

[164] T. Mitsui, *Jap. Analyst*, 1953, **2**, 117.

[165] Y. Okada and H. Hanafusa, *Bull. Chem. Soc., Japan*, 1954, **27**, 478.

[166] B. W. Grunbaum, P. L. Kirk, L. G. Green, and C. W. Koch, *Analyt. Chem.*, 1955, **27**, 384.

[167] P. R. W. Baker, *Analyst*, 1955, **80**, 481.

[168] J. P. Dixon, *Analyt. Chim. Acta*, 1955, **13**, 12.

[169] S. Ohashi, *Bull. Chem. Soc. Japan*, 1955, **28**, 177.

[170] O. Mikl and J. Pech, *Chem. Listy*, 1953, **47**, 904.

The sample is wrapped in filter-paper which is ignited and lowered into a flask filled with oxygen, acid gases being absorbed in hydrogen peroxide. The sulphuric acid formed is titrated with standard alkali. If chlorine is present it is determined by titrating the neutralised solution with mercuric nitrate.

A similar method has been described by Schöniger [171] for the determination of chlorine and bromine, which are finally determined by the mercuric oxycyanide method.

Sulphur has been determined by combustion in an empty tube with chromic oxide as catalyst.[172] Sulphur oxides are absorbed on sodium silicate contained in a boat which presumably is then weighed. Vecera [173] claims to have improved the so-called Zinneke method by using a 10-cm. length of silver shavings kept at 450—480° to absorb sulphur oxides, the sample being burnt in the usual way over a platinum contact. Silver sulphate is extracted with water and titrated potentiometrically with 0·01N-potassium iodide solution.

To overcome low results due to the fixation of sulphur when metals are present, Sirotenko [174] recommends covering the residue in the boat after the combustion, with boron oxide and re-igniting it. The sulphur oxides produced are absorbed and titrated in the usual way.

A method has been described [175] for the determination of 1—100 p.p.m. of sulphur in organic liquids, in which the sample is decomposed in a vertical furnace packed with vanadium pentoxide and the sulphur formed is measured by a conductometric method.

Chlorine in certain chlorinated aromatic compounds has been determined by hydrolysis in a solution of potassium hydroxide in tetrahydrofurfuryl alcohol.[176] The alcohol is distilled off and the residual solution is titrated by Volhard's method.

Brown and Musgrave [177] determine fluorine, chlorine, and nitrogen simultaneously by decomposition with sodium in a nickel bomb. When oxygen is absent from the compound, nitrogen is converted quantitatively into cyanide. Fluorine is determined on one aliquot part by means of a thorium nitrate titration, chlorine on another part by argentometric titration using Rhodamine-BS indicator, and cyanide on a further part by the Liebig–Denigès method. In a later paper [178] an ion-exchange method is reported for chlorine and fluorine after masking cyanide with formaldehyde. The total acidity of the eluate is determined, and chloride then titrated argentometrically or by the mercury oxycyanide method.

Raney nickel in an alkaline medium or zinc–sulphuric acid in the presence of palladised charcoal has been recommended as an alternative to the usual methods of decomposition for the determination of halogens.[179] The particular reagent to be used depends on the nature of the compound.

Fluorine has also been determined on the semimicro-scale after

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[171] W. Schöniger, *Mikrochim. Acta*, 1955, 123.
[172] P. N. Fedoseev and R. M. Lagoschnaya, *Zhur. analit. Khim.*, 1954, **9**, 224.
[173] M. Večeřa, *Chem. Listy*, 1954, **48**, 613.
[174] A. A. Sirotenko, *Mikrochim. Acta*, 1955, 153.
[175] J. A. Hudy and R. D. Mair, *Analyt. Chem.*, 1955, **27**, 802.
[176] E. H. Searle and E. Bell, *J. Appl. Chem.*, 1954, **4**, 430.
[177] F. Brown and W. K. R. Musgrave, *Analyt. Chim. Acta*, 1955, **12**, 29.
[178] R. E. Banks, F. Cuthbertson, and W. K. R. Musgrave, *ibid.*, 1955, **13**, 442.
[179] L. Simonyi, G. Tokáv, and G. Gál, *Magyar Kém. Folyóirat*, 1954, **60**, 97.

decomposition in a Parr bomb by passing the leachings through an ion-exchange resin before titration with thorium nitrate in the usual way.[180]

Fluorine and carbon have been determined simultaneously by decomposition in a silica tube in the presence of moist oxygen at 1100°.[181] The hydrofluoric acid produced is titrated with standard alkali and the carbon dioxide is determined gravimetrically after absorption in a soda-asbestos tube.

Burton and Riley [182] have described a rapid method for the determination of phosphorus in which the samples are decomposed in a Parr micro-bomb and then determined spectrophotometrically by the molybdenum-blue method.

Arsenic can be determined rapidly by heating in a sealed tube for 5 minutes with magnesium and magnesium oxide.[183] The contents of the tube are decomposed with dilute acid and the evolved arsine is trapped in a solution of silver diethyldithiocarbamate in pyridine. The colour produced is measured spectrophotometrically. Pietsch [184] decomposes by wet digestion, adds barium nitrate, and determines arsenate in the filtrate by the Volhard method. It is claimed that the method can be applied in the presence of many metals and halogens.

A modified wet oxidation method for 10-mg. samples has been developed which avoids the low results sometimes obtained when sulphuric-nitric acid oxidation is used.[185] The sample is dissolved in sulphuric acid and oxidised with potassium permanganate, the excess of which is removed with hydrogen peroxide. After evaporation to fumes of sulphuric acid, the conventional iodometric titration is applied.

A new combustion procedure to determine mercury when halogens are present, which eliminates possible loss as mercury halide, has been described.[186] The combustion tube is packed with calcium oxide, and mercury is collected in a bubbler containing nitric acid. It is finally titrated with potassium thiocyanate, ferric alum being used as indicator.

Methoxyl and ethoxyl groups have been determined selectively by the trimethylamine method, *iso*propanol being used as solvent in place of the usual ethanol.[187] No solubility correction for tetramethylammonium iodide is then necessary. The latter is filtered off and ethoxyl is then determined in the filtrate.

A critical study of the methoxyl determination has been carried out.[188] Erratic results were traced to the use of sodium thiosulphate in the scrubber. When 25% sodium acetate solution was used instead, satisfactory results were obtained. In an independent study [189] sodium antimonyl tartrate was found to be the best of several scrubbing solutions which were examined.

A new improved apparatus has been described by Kirsten and Ehrlich-

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[180] C. Eger and A. Yarden, *Bull. Res. Council Israel*, 1954, **4**, 305.

[181] H. E. Freier, B. W. Nippoldt, P. B. Olsen, and D. G. Weiblen, *Analyt. Chem.*, 1955, **27**, 146.

[182] J. D. Burton and J. P. Riley, *Analyst*, 1955, **80**, 391.

[183] M. Jureček and J. Jenik, *Coll. Czech. Chem. Comm.*, 1955, **20**, 550.

[184] R. Pietsch, *Z. analyt. Chem.*, 1955, **144**, 353.

[185] G. Bähr, H. Bieling, and K. H. Thiele, *Z. analyt. Chem.*, 1954, **143**, 103.

[186] T. Sudo, D. Shimoe, and F. Miyahara, *Jap. Analyst*, 1955, **4**, 88.

[187] G. Gran, *Svensk. Papperstidning*, 1954, **57**, 702.

[188] A. E. Heron, R. H. Read, H. E. Stagg, and H. Watson, *Analyst*, 1954, **79**, 671.

[189] R. Belcher, J. E. Fildes, and A. J. Nutten, *Analyt. Chim. Acta*, 1955, **13**, 16.

Rogozinsky.[190] The sample is first heated with the reaction mixture in a stoppered tube for 30 minutes at 100° and is then transferred to the apparatus to distil off the methyl iodide. The determination is completed iodometrically.

R. B.

Polarography.

Inorganic.—During the period covered by this Report, considerable attention has been paid to the selection of electrode systems for use in polarographic analysis. A vibrating platinum electrode has been chosen for the determination of oxygen in water.[191] The diffusion current varies as the square root of the amplitude, and is greater than that obtained with a rotating electrode. A value of 50 c.p.s. was chosen as normal. Platinum micro-electrodes and automatic recording have been used for polarography in fused salts, and the effects of variation in speed of rotation, electrode area, and temperature on the rate of polarisation have been studied.[192] A new type of mercury electrode which has a pinhole small enough to prevent mercury (kept at constant pressure level) from falling has been described.[193] The sensitivity is comparable to that of the dropping electrode, and the polarograms are smooth with considerably less slope than those obtained with the streaming electrode. Yet another form of dropping-mercury cathode, in which the end is bent into a horizontal position, has been devised. The advantage claimed is that the mercury drop has minimum size and maximum stability. Reduction in dropping time minimises galvanometer oscillation.[194] The dropping-gallium electrode has been found entirely unsuitable.[195] The advantages of replacing the calomel and other conventional reference electrodes by electrodes such as antimony, molybdenum, tungsten, graphite, etc., when the limiting current rather than the half-wave potential is being measured, have been discussed. These electrodes simplify vessel design, and give excellent waves.[196] A nomogram for determining the characteristics of capillaries has been constructed.[197] Japanese authors [198] have described a polarograph in which a small alternating current is superimposed on the directly applied potential, and the alternating current is recorded directly on photographic paper. The method was applied to several analyses and theoretical implications were considered. A general discussion of the various methods of oscillographic polarography has been published,[199] and its application in quantitative analysis has been treated.[200] The excellence of the Barker " Square Wave " polarograph has been demonstrated, particularly in respect to sensitivity and selectivity.[201]

[190] W. Kirsten and S. Ehrlich-Rogozinsky, *Mikrochim. Acta*, 1955, 786.
[191] W. Dirschel and K. Otto, *Chem.-Ind.-Tech.*, 1954, **26**, 321.
[192] E. D. Black and T. De Vries, *Analyt. Chem.*, 1955, **27**, 906.
[193] Y. Yashiro, *Bull. Chem. Soc. Japan*, 1954, **27**, 564.
[194] J. Smoller, *Coll. Czech. Chem. Comm.*, 1954, **19**, 238.
[195] P. A. Giguère and D. Lamontagne, *Science*, 1954, **120**, 390.
[196] L. Jensovšký, *Chem.-Tech., Berlin*, 1955, **7**, 159.
[197] D. P. Schcherbov, *Zavodskaya Lab.*, 1955, **21**, 246.
[198] M. Senda, M. Okuda, and I. Tachi, *Bull. Chem. Soc. Japan*, 1955, **28**, 31, 37.
[199] Ya. P. Gokhshtein and Yu. A. Surkov, *Zhur. analit. Khim.*, 1954, **9**, 319.
[200] R. Kalvoda and J. Macku, *Chem. Listy*, 1954, **48**, 378.
[201] D. J. Ferrett and G. W. C. Milner, *Analyst*, 1955, **80**, 132.

Attention has been drawn to the non-proportionality between concentration and maximum current in derivative polarography.[202] The effect of adsorption on the anodic polarographic wave has been studied,[203] and attention has been paid to selection of the zero line in cases where an incomplete wave is obtained.[204] Methods have been specified for the purification of supporting electrolytes for use in polarography.[205]

Very many analytical methods have been described during the past year. Few outstanding applications have appeared and it is only possible to mention some of the more interesting methods. The suitability of ascorbic acid, phthalic acid, and benzoic acid media for the determination of uranium has been examined.[206] Ascorbic acid appears to be the most efficient base electrolyte.[207] Others have used an ammonium carbonate medium containing "Tiron" (1 : 2-dihydroxybenzene-3 : 5-disulphonic acid) and complexone III (E.D.T.A.) for the same analysis. Methods for the determination of zinc in various electrolyte media and in various alloys, ores, etc., have been investigated.[208] The polarography of niobium has been described [209-211] and also that of thallium,[212,213] gallium,[214] indium,[215] palladium,[216] and gold.[217,218] The polarographic determination of copper [219] and of cadmium and zinc [220] in cyanide solution has been investigated, and also general applications of the method to the analysis of electroplating solutions.[221] The polarographic method is well suited to the analysis of minor constituents in titanium alloys.[222] *m*-Nitrophenylarsonic acid has been described as a polarographic reagent for the latter metal.[223] After precipitation of the titanium compound, it is dissolved and the nitro-group is polarographed. The polarographic behaviour of chlorides,[224] bromides,[225] chlorates,[226] sulphate,[227] sulphite,[228] nitrate and nitrite,[229,230] fluoride,[231]

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[202] T. Isshiki, Y. Mashiko, and S. Tsukagoshi, *Pharm. Bull., Japan*, 1954, **2**, 263.

[203] P. Zuman, *Chem. Listy*, 1954, **48**, 1025.

[204] N. Z. Bruja, *Rev. Chim.*, 1953, **4**, 30.

[205] L. Meites, *Analyt. Chem.*, 1955, **27**, 416.

[206] M. V. Šušić, *Bull. Inst. Nuclear Sci. Belgrade*, 1954, **4**, 57, 59.

[207] M. V. Šušić, I. Gal, and E. Cuker, *Analyt. Chim. Acta*, 1954, **11**, 586.

[208] I. A. Korshunov, *Uch. Zap. Gor'kovskogo Un-Ta*, 1953, **24**, 15.

[209] S. K. Dhar, *Analyt. Chim. Acta*, 1954, **11**, 289.

[210] D. J. Ferrett and G. W. C. Milner, *Nature*, 1955, **175**, 477.

[211] E. I. Krylor, U. S. Kolevatova, and V. A. Samarina, *Doklady Akad. Nauk S.S.S.R.*, 1954, **98**, 593.

[212] A. A. Vleck, *Chem. Listy*, 1954, **48**, 189.

[213] G. W. Smith and F. Nelson, *J. Amer. Chem. Soc.*, 1954, **76**, 4714.

[214] H. E. Zittel, *Diss. Abs.*, 1954, **14**, 1303.

[215] M. Bulovova, *Chem. Listy*, 1954, **48**, 655.

[216] R. F. Wilson and R. C. Daniels, *Analyt. Chem.*, 1955, **27**, 904.

[217] J. Cihalik, J. Dolezal, V. Simon, and J. Zyka, *Chem. Listy*, 1954, **48**, 28.

[218] J. Kracek, *Cesk. Sklar a Keramik*, 1953, **3**, 183.

[219] J. V. Petrocelli and G. Tatoian, *Plating*, 1955, **42**, 550.

[220] T. A. Downey, *ibid.*, p. 267.

[221] R. Diaz, *ibid.*, p. 415.

[222] J. J. Mikula and M. Codell, *Analyt. Chem.*, 1955, **27**, 729.

[223] E. Van Dalen and R. P. Graham, *Analyt. Chim. Acta*, 1955, **12**, 489.

[224] A. A. Vleck, *Coll. Czech. Chem. Comm.*, 1954, **19**, 221.

[225] M. Hemala, *Chem. Listy*, 1953, **47**, 1323.

[226] J. Koryta and J. Tenygl, *ibid.*, 1954, **48**, 407.

[227] O. A. Ohlweiler, *Analyt. Chim. Acta*, 1954, **17**, 590.

[228] V. B. Aulenbach and J. L. Balmat, *Analyt. Chem.*, 1955, **27**, 562.

[229] R. Pletikha and E. Krzhizhova, *Zhur. analit. Khim.*, 1954, **9**, 366.

[230] *Idem*, *Prumysl. Potravin*, 1953, **4**, 383.

[231] C. E. Shoemaker, *Analyt. Chem.*, 1955, **27**, 552.

iodine and iodides[232] has been studied. Methods have been described for manganese in air,[233] tin in ores,[234] dissolved oxygen and hydrogen peroxide,[235] and for minute amounts of carbon monoxide.[236]

Amperometric methods have been proposed for several analyses, *e.g.*, of ferricyanide with silver nitrate,[237] of thorium with fluoride,[238] of zirconium in fluoride medium with cupferron,[239] of calcium and fluoride[240] (indirectly *via* calcium), and also of lead[241] with ferrocyanide, of heavy metals with sodium hydroxide by use of a rotating platinum electrode,[242] of arsenite, ammonia, and thiocyanate with hypochlorite,[243] of copper and nickel in alloy steel by means of rubeanic acid,[244] of copper, zinc, nickel, and cobalt with sodium anthranilate,[245] of copper with sodium carbonate by use of copper electrodes (this procedure is said to be superior to the use of the dropping-mercury cathode or rotating platinum cathode).[246] Perhaps the most interesting amperometric method to be suggested during the period is that for the determination of potassium.[247] The potassium is precipitated with sodium tetraphenylboron, and the excess reagent is then titrated with thallous nitrate. Apart from the similar behaviour of rubidium, cæsium, and ammonium, chloride is said to interfere.

Organic.—A general review of the polarographic method and instruments in general has been made[248] and particular attention has been paid to organic applications of the technique.[249] Studies have been made of the polarography of steroids,[250] sulphur compounds,[251] aromatic heterocyclic compounds,[252] ethers and esters.[253] Many workers continue to pursue the line of functional group analysis by means of polarography and amperometric titration. Examples are the determination of the carbonyl group,[254] aliphatic nitro-groups,[255] disulphide,[256] sulphones,[257] and thiols.[258] Extensive surveys have been made of the polarography of several compounds:

[232] J. V. A. Novák, *Chem. Listy*, 1953, **47**, 903.
[233] I. B. Kogan and S. L. Makhover, *Gigiena i Sanit.*, 1954, **2**, 52.
[234] L. Bouberlova-Kosinova, *Vest. Ustred Ustav. Geol.*, 1954, **29**, 13.
[235] J. C. Fittipaldi, *Rev. Fac. Ing. Quím. argentina*, 1953, **21—22**, 123.
[236] J. Vykoukal and K. Linhart, *Paliva*, 1953, **33**, 236.
[237] B. Khosla and H. C. Gaur, *Current Sci.*, 1954, **23**, 216.
[238] M. Sundaresan and M. D. Karkhanavala, *ibid.*, p. 258.
[239] E. C. Olson and P. J. Elving, *Analyt. Chem.*, 1954, **26**, 1747.
[240] O. A. Songina, A. P. Voiloshnikova, and M. T. Kozlovskii, *Izvest. Akad. Nauk Kazakhstan S.S.R.*, 1953, *Ser. Khim.* [6], 69.
[241] B. Khosla, H. C. Gaur, and N. P. Ramaiah, *Current Sci.*, 1954, **23**, 361.
[242] J. Kamecki and M. Slabon, *Roczniki Chem.*, 1955, **29**, 107.
[243] H. A. Laitinen and D. E. Woerner, *Analyt. Chem.*, 1955, **27**, 215.
[244] Kh. Ya. Levitman and Z. A. Krivchik, *Zavodskaya. Lab.*, 1955, **21**, 397.
[245] A. K. Zhdanov, R. I. Tseitlin, and A. M. Yakubov, *ibid.*, p. 7.
[246] J. Kamecki and L. Suski, *Roczniki Chem.*, 1955, **29**, 115.
[247] W. Kemula and J. Kornacki, *ibid.*, 1954, **28**, 635.
[248] W. van Tongeren, *Chem. Weekblad*, 1954, **50**, 769.
[249] F. Freese, *ibid.*, p. 781.
[250] M. Brezina, V. Volkova, and J. Volke, *Chem. Listy*, 1954, **48**, 194.
[251] P. Zuman, R. Zumanova, and J. Teisinger, *Coll. Czech. Chem. Comm.*, 1955, **20**, 139.
[252] J. Volke and V. Volkova, *Chem. Listy*, 1954, **48**, 1031.
[253] M. I. Bobrova and A. N. Matregeva, *Zhur. obshchei Khim.*, 1954, **24**, 1741.
[254] Ch. Prévost and P. Souchay, *Chim. analyt.*, 1955, **37**, 3.
[255] R. Miquel and A. Condylis, *Bull. Soc. chim. France*, 1955, 236.
[256] J. R. Carter, *Science*, 1954, **120**, 895.
[257] E. S. Levin, A. P. Shestov, *Doklady Akad. Nauk S.S.S.R.*, 1954, **96**, 999.
[258] M. D. Grimes, J. E. Puckett, B. J. Newby, and B. J. Heinrich, *Analyt. Chem.*, 1955, **27**, 152.

barbituric acid derivatives,[259, 260] penicillin,[261] papaverine,[262] chlorophyllins,[263] cystine,[264] dithiocarbamic acids,[265] oxalic acid,[266] maleic anhydride,[267] formaldehyde,[268] aureomycin and terramycin,[269] the lower alkyl, dialkyl, and acyl peroxides,[270] alkyl phthalate esters,[271] amaranth,[272] *cyclo*hexyldinitrophenols,[273] diethyldithiocarbamate,[274] and di- and triphosphopyridine nucleotides.[275] In addition, the polarographic assay of technical malathion [276] (*S*-1 : 2-dicarbethoxyethyl-*OO*-dimethyl dithiophosphate), trypsin activity,[277] ethyl alcohol content of blood,[278] thio-compounds in blood and serum,[279] and of carbon oxysulphide [280] has been described. The role of polarography in biochemistry [281] and of oscillographic polarography in pharmacy has been reviewed generally.[282]

Potentiometric Titration.—The selection of the inflection point on potentiometric titration curves by the concentric-arcs method using a simply made transparent template is described by Tubbs.[283] The well-known ability of a platinum electrode to respond to changes of silver-ion concentration has been examined.[284] The response was found to be due to a layer of silver formed at the interface and it varied with the previous treatment of the electrode. The discussion also covers the similar behaviour of gold and carbon electrodes. It has been shown [285] that, in the titration of ferrous iron with ceric sulphate, a platinised platinum electrode may function partly as an oxygen electrode when the concentration of ferrous ion is less than 0·001M. A study [286] has been made of the response of a silver electrode to pH, with the conclusion that it is not suitable for the determination of pH although a linear relationship between potential and pH was obtained from pH 2 to 9. The precipitation of halides with silver nitrate has been studied with a glass electrode.[287] The curves for direct titration against silver nitrate have maxima at the equivalence point and the reverse titration

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[259] P. Zuman, *Chem. Listy*, 1954, **48**, 1006.
[260] *Idem, ibid.*, p. 1020.
[261] E. Krejci, *Cesk. Farm.*, 1955, **4**, 73.
[262] V. D. Bezuglyi, *Zhur. obshchei Khim.*, 1954, **24**, 2190.
[263] W. L. Waggatzer and J. E. Christian, *J. Amer. Pharm. Assoc., Sci. Edn.*, 1955, **94**, 30.
[264] M. Kalousek, O. Grubner, and A. Tockstein, *Coll. Czech. Chem. Comm.*, 1954, **19**, 1111.
[265] R. Zahradník and L. Jenšovský, *Chem. Listy*, 1954, **48**, 11.
[266] G. F. Reynolds and R. C. Smart, *Analyt. Chim. Acta*, 1954, **11**, 487.
[267] E. Barendrecht, *Chem. Weekblad*, 1954, **50**, 785.
[268] L. Séràk, *Chem. Listy*, 1954, **48**, 272.
[269] O. Tělupilová and V. Mašinová, *Cesk. Farm.*, 1953, **2**, 226.
[270] H. Brüschweiler and G. J. Minkoff, *Analyt. Chim. Acta*, 1955, **12**, 186.
[271] G. C. Whitnack, J. Reinhart, and E. St. Clair Gantz, *Analyt. Chem.*, 1955, **27**, 359.
[272] G. C. McKeown and J. L. Thompson, *Canad. J. Chem.*, 1954, **32**, 1025.
[273] M. Maruyama and K. Maruyama, *Jap. Analyst*, 1954, **3**, 11.
[274] J. Davis, A. J. Easton, and J. Freezer, *Chem. and Ind.*, 1955, 241.
[275] C. Carruthers and J. Tech, *Arch. Biochem. Biophys.*, 1955, **56**, 441.
[276] W. H. Jura, *Analyt. Chem.*, 1955, **27**, 525.
[277] Š. Stokrova, *Chem. Listy*, 1954, **48**, 1082.
[278] D. Monnier and W. F. Rüedi, *Helv. Chim. Acta*, 1955, **38**, 402.
[279] L. Jirousek and M. Petrackova, *Chem. Listy*, 1954, **48**, 260.
[280] V. Sedivec and V. Vašák, *ibid.*, p. 19.
[281] J. de Wael, *Chem. Weekblad*, 1954, **50**, 778.
[282] J. Heyrovský, *Cesk. Farm.*, 1953, **2**, 403.
[283] C. F. Tubbs, *Analyt. Chem.*, 1954, **26**, 1670.
[284] P. L. Allen and A. Hickling, *Analyt. Chim. Acta*, 1954, **11**, 467.
[285] T. de Vries, *Chem. Weekblad*, 1954, **50**, 533.
[286] H. Khalifa and I. M. Issa, *J. Indian Chem. Soc.*, 1954, **31**, 426.
[287] W. Hubicki, *Ann. Univ. M. Curie-Sklodowska*, 1953, **8**, 149.

curves have minima. The addition of indifferent electrolytes decreases step height. Potentiometric titrations with controlled current input have been described by Adams,[288] but he has concluded that the new method is frequently no better than conventional potentiometry except that sometimes larger inflexions are obtained. It has been found that a platinum electrode immersed in a solution containing hydrogen peroxide changes its potential linearly with pH.[289] The electrode can be used for the titration of acids, bases, and certain salts and was applied to the determination of active chlorine, alkali, and carbonate in hypochlorites and chlorites. It was subsequently used for the titration of dichromate ions and strong acids when present together.[290]

Potentiometric methods have been described for the titration of low concentrations of boric acid in water and deuterium oxide. The titration was carried out with carbonate-free potassium hydroxide with addition of mannitol. Helium gas was used for stirring.[291] Mannitol was preferred to glycerol. Other authors have confirmed that invert sugar, fructose, propane-1 : 2-diol, and ethylene glycol can also replace glycerol. These authors [292] preferred ethylene glycol to mannitol. Maltose, lactose, starch, dextrin, etc., were ineffective. Quadrivalent selenium can be titrated with potassium permanganate in a sodium hydroxide medium.[293] A new potentiometric method has been described for cadmium in which the latter is precipitated as $(C_{22}H_{24}O_2N_4)_2H_2[CdBr_4]$ by addition of diantipyrinylmethane in the presence of a known amount of 0·2N-potassium bromide. The excess of bromide ion is then determined argentometrically.[294] A potential drop of approximately 400 mv was recorded by others for the potentiometric titration of hydrogen peroxide with 0·1N-potassium ferricyanide in alkaline medium.[295] Singh *et al.*[296] have continued their studies on the use of chloramine-B by describing the potentiometric determination of ferrocyanide, hydrazine, ferrous sulphate, iodide, arsenic(III), antimony(III), quinol, and quinhydrone. The titrations were carried out in dilute mineral acid. The potentiometric determination of sulphur in a wide variety of materials has been described,[297] and the titration of thiols and disulphides by means of silver nitrate has been critically examined, errors in previous work being disclosed.[298] Others have described the automatic pH titration of soluble phosphates and their mixtures.[299] A mean-square error of ±1·9% has been recorded for the potentiometric determination of sodium fluoride by titration against an aluminium salt with the quinhydrone electrode.[300] Deschamps's method for the potentiometric titration of

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[288] R. N. Adams, *Analyt. Chem.*, 1954, **26**, 1933.

[289] I. E. Flis, *Zhur. analit. Khim.*, 1954, **10**, 38.

[290] I. E. Flis and Zh. L. Vert, *ibid.*, p. 44.

[291] L. Silverman and W. Bradshaw, *Analyt. Chim. Acta*, 1955, **12**, 177.

[292] J. J. Sciarra and J. A. Zapotocky, *J. Amer. Pharm. Assoc., Sci. Edn.*, 1955, **44**, 370.

[293] I. M. Issa, S. A. Eid, and R. M. Issa, *Analyt. Chim. Acta*, 1954, **11**, 275.

[294] V. P. Zhivopistsev, *Uch. Zap. Molotovskogo, Gos. Un-ta*, 1953, **8**, 141.

[295] J. Vulterin and J. Zýka, *Chem. Listy*, 1954, **48**, 619.

[296] B. Singh and G. Singh, *Analyt. Chim. Acta*, 1954, **11**, 569.

[297] G. Graus and A. Zöhler, *Angew. Chem.*, 1954, **66**, 437.

[298] R. Cecil and J. R. McPhee, *Biochem. J.*, 1955, **59**, 234.

[299] J. R. van Wazer, E. J. Griffith, and J. F. McCullough, *Analyt. Chem.*, 1954, **26**, 1755.

[300] Sh. T. Talipov and I. L. Teodorovich, *Doklady Akad. Nauk Uzbekhistan S.S.R.*, 1953, 32.

chlorides in sea water in an aqueous acetone medium has been favourably reviewed by Denamur.[301] A copper indicator electrode has been used for the potentiometric titration of xanthates with standard copper sulphate solution.[302]

Conductometric Titration.—During this period relatively little work has been done on the application of conductometric titration techniques to analytical problems. The design of cells for precision conductometry has been discussed.[303] Japanese authors have reported on the conductometric titration of copper with a 0·05M-solution of 8-hydroxyquinoline in ethanol,[304] and another worker [305] has determined the chloride content of serum by titration with silver nitrate after precipitation of protein with alcohol. Higuchi *et al.*[306] have titrated hydrochloric and sulphuric acids and their mixtures in anhydrous acetic acid, with a standard lithium acetate reagent. The curves showed distinct breaks corresponding to Cl^-, $SO_4^{=}$, and HSO_4^-. The relative merits of lithium, sodium, potassium, and tripentylammonium acetates as titrants were examined. Conductometric and potentiometric techniques have been compared for the titration of free acids and of acids liberated by hydrolysis from nickel(II) salts at high temperatures.[307] The conductometric titration of anabasine and lupinine mixtures in acetone solution against 0·05N-mineral acid or naphthalene-2-sulphonic acid has been reported. The latter titrant gave the most satisfactory results.[308]

High-frequency Titration.

The fundamentals of high-frequency titration and specifically the properties of analysers "without electrode contact" have been discussed particularly with reference to measurements with a heterodyne apparatus.[309] A study has been made of the mechanism of high-frequency titration methods by means of a "Q meter" [310] and the relationship between the resistance and the concentration of the solution and its application to the explanation of titration curves, have been discussed in detail.[311] The same author has also examined the general theory of high-frequency titrations.[312] Other authors [313] have independently examined the change in electrical characteristics of solutions during titration.

Ethylenediaminetetra-acetic acid has been used as a titrant for the high-frequency determination of several cations. Hara and West [314] have used the Sargent Model V Oscillometer for chelation studies of several ions,

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[301] J. Denamur, *Compt. rend.*, 1955, **240**, 1223.

[302] M. Oktawiec, *Prace Inst. Minist. Hutnic*, 1954, **5**, 184.

[303] J. C. Nichol and R. M. Fuoss, *J. Phys. Chem.*, 1954, **58**, 696.

[304] K. Shinra, K. Yoshikawa, T. Kato, and Y. Nomizo, *J. Chem. Soc. Japan*, 1954, **75**, 46.

[305] H. A. Teloh, *Amer. J. Clin. Path.*, 1954, **24**, 1095.

[306] T. Higuchi and C. R. Rehm, *Analyt. Chem.*, 1955, **27**, 408.

[307] F. Cuta, Z. Ksandr, and M. Hejtmánek, *Chem. Listy*, 1954, **48**, 1341.

[308] V. V. Udovenko and L. A. Vvedenskaya, *Trudy Sredneaziatskogo Gosudarst Univ. Khim. Nauk*, 1953, **40**, 3.

[309] K. Cruse and R. Huber, *Angew. Chem.*, 1954, **66**, 625.

[310] M. Honda, K. Nakano, and A. Satuka, *J. Chem. Soc. Japan*, 1954, **75**, 1299.

[311] K. Nakano, *ibid.*, p. 773.

[312] *Idem*, *ibid.*, p. 776.

[313] V. A. Zarinskii and D. I. Koshkin, *Zhur. analit. Khim.*, 1955, **10**, 110.

[314] R. Hara and P. W. West, *Analyt. Chim. Acta*, 1954, **11**, 264.

particularly uranyl ion at pH 3·5—4·0,[315] and bivalent metals such as nickel, cobalt, manganese, zinc, cadmium, and lead. Calcium was titrated successfully in the presence of a phosphate buffer, but magnesium and the other alkaline earths gave erratic results.[316] Large concentrations of electrolyte disturbed these titrations. High-frequency titrations of the salts of various organic acids in non-aqueous solvents have been reported.[317] Sodium salts were directly titrated with perchloric acid, and potassium salts were back-titrated by using sodium acetate in glacial acetic acid.

Coulometric Titrations.

Coulometric determinations at constant current in unstirred solutions have been described by Gierst *et al.*[318] In this method only the transition time is measured, *i.e.*, the interval between the establishment of capacity charge on the electrode and the increase in potential that occurs when the concentration of the substance at the surface of the electrode falls to zero. The subject is treated mathematically, and two transitometers are described for providing the necessary electrical and timing devices. Determinations occupy less than one minute and the accuracy is approx. 0·2%. Lingane [319] has described a method and electrode assembly for the automatic coulometric titration of acids. Another author [320] has examined the various stages in the titration of a solution of hydrochloric acid by coulometry at constant intensity. Salicylic acid has been determined coulometrically by bromination and amperometric titration of the excess generated with cuprous ion.[321] Electrically generated bromine has also been used for the titration of phenols.[322] Here, however, the reaction was sufficiently rapid to permit direct determination. Selenium(IV) has been determined coulometrically with iodide and thiosulphate.[323] Chloride, bromide, and iodide have been titrated coulometrically with electrically generated silver ion, dichlorofluorescein being used as indicator.[324] Concentrations of lead down to 10^{-8}M have been analysed by coulometric technique.[325] Various dyes have been titrated coulometrically with externally generated titanous ion,[326] and electrically generated permanganate [327] has been used to determine oxalate, ferrous iron, and arsenite.

Photometric Titration.

Underwood [328] has discussed the technique, apparatus, and applications of photometric titrations. The applications are discussed in a general way

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[315] R. Hsra, and P. W. West, *Analyt. Chim. Acta*, 1955, **12**, 285.
[316] *Idem, ibid.*, p. 72.
[317] M. Ishidate and M. Masui, *Pharm. Bull., Japan*, 1954, **2**, 50.
[318] L. Gierst and P. Mechelynik, *Analyt. Chim. Acta*, 1955, **12**, 79.
[319] J. J. Lingane, *ibid.*, 1954, **11**, 283.
[320] J. Badoz-Lambling, *Chim. analyt.*, 1954, **36**, 291.
[321] B. Kawamura, K. Momoki, and S. Suzuki, *Jap. Analyst*, 1954, **3**, 29.
[322] C. N. Van Zyl and K. A. Murray, *S. African Ind. Chemist*, 1954, **8**, 243.
[323] K. Rowley and E. H. Swift, *Analyt. Chem.*, 1955, **27**, 818.
[324] P. S. Tutundzic, I. Doroslovacki, and O. Tatic, *Analyt. Chim. Acta*, 1955, **12**, 481.
[325] T. L. Marple and L. B. Rogers, *ibid.*, 1954, **11**, 574.
[326] J. S. Parsons and W. Seaman, *Analyt. Chem.*, 1955, **27**, 210.
[327] P. S. Tutundzic and S. Mladenovic, *Analyt. Chim. Acta*, 1955, **12**, 390.
[328] A. L. Underwood, *J. Chem. Educ.*, 1954, **31**, 394.

in respect of acid–base, redox, precipitation, and complexometric titrations. Stress is laid on the use of ethylenediaminetetra-acetic acid in complex-formation titrations. Automatic spectrophotometric titrations with coulometrically generated titanous ion have been used for the determination of vanadium in titanic chloride.[329] Bobtelsky *et al.* have continued their studies of the heterometric technique by using quinaldic acid for the titration of copper in the presence of sundry other metals,[330] and 1-nitroso-2-naphthol for the determination of ferric iron [331] and cobalt.[332, 333] Other workers [334] have described the automatic photometric titration of calcium and magnesium in carbonate rocks, using ethylenediaminetetra-acetic acid with the usual murexide and Eriochrome-black T indicators.

Flame Photometry.

As would be expected, during the period of the Report, the bulk of papers having the use of the flame photometer as their main subject matter are concerned with the analysis of small amounts of the alkali and alkaline-earth metals. A few papers deal with the determination of other ions. Thus, attention has been paid to the determination of copper in gasoline, after extraction with hydrochloric acid; [335] to the determination of boron [336] by using an aqueous methanol solvent (1 : 1) which is 0·5M in hydrochloric acid, to the determination of lanthanum [337] by use of the band spectra of LaO, and to the determination of amino-nitrogen by the ingenious device of shaking the amino-acid solution with a suspension of copper phosphate and subsequently determining the chelate-bound copper by the flame photometer.[338]

Various workers have reported on the determination of sodium: in pure solution,[339] and in alumina [340] in the presence of calcium [341] and the other alkaline earths,[342] in glass and ores,[343] and in rocks.[344] Potassium has been determined: in fertilisers after ion-exchange separation [345] of interfering anions, in the presence of sodium,[346, 343, 344] and in the presence of alkaline-earth metals.[342] Methods have been described for lithium [342, 343] and for rubidium and cæsium.[343] Methods for overcoming interference in the

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[329] H. V. Malmstadt and C. B. Roberts, *Analyt. Chem.*, 1955, **27**, 741.
[330] M. Bobtelsky and B. Graus, *Analyt. Chim. Acta*, 1954, **11**, 253.
[331] M. Bobtelsky and E. Jungreis, *ibid.*, 1955, **12**, 351.
[332] *Idem, ibid.*, p. 248.
[333] *Idem, ibid.*, p. 263.
[334] L. Shapiro and W. W. Brannock, *Analyt. Chem.*, 1955, **27**, 725.
[335] J. H. Jordan, *Petrol Refining*, 1954, **33**, 158.
[336] J. A. Dean and C. Thompson, *Analyt. Chem.*, 1955, **27**, 42.
[337] R. Ishida, *J. Chem. Soc. Japan*, 1955, **76**, 60.
[338] R. E. Beauchene, A. D. Berneking, W. G. Schrenk, H. L. Mitchell, and R. E. Silker, *J. Biol. Chem.*, 1955, **214**, 731.
[339] F. Hegemann, V. Caimann, and H. Zoellner, *Ber. deutsch. keram. Ges.*, 1954, **31**, 315.
[340] A. Hegedas, F. K. Fukker, and M. Dvorszky, *Magyar Kém. Folyóirat*, 1953, **59**, 334.
[341] F. Hegemann and B. Pfab, *Glastechn. Ber.*, 1954, **27**, 189.
[342] W. Schuhknecht and H. Schinkel, *Z. analyt. Chem.*, 1954, **143**, 321.
[343] J. P. Williams and P. B. Adams, *J. Amer. Ceram. Soc.*, 1954, **37**, 306.
[344] L. Jenkins, U.S. Atomic Energy Comm., TEI–453, 1954.
[345] C. W. Gehrke, H. E. Affsprung, and E. L. Wood, *J. Agric. Food Chem.*, 1955, **3**, 48.
[346] R. Neumann, *Gas Lek Ces.*, 1954, **93**, 1229.

determination of sodium and potassium due to overlapping spectra, radiation, and anions have been discussed.[347] The interference of chlorohydrocarbons owing to flame quenching has been reported by Milton and Duffield.[348] Another worker [349] has reported on the influence of the stability of the light source and the mutual effects of sodium and potassium on each other. Methods have been reported for the determination of calcium in the presence of the other alkaline earths,[350] in natural waters,[351] and in serum.[352] An acetylene flame has been used for the photometric determination of strontium [353] without interference from iron, sodium, calcium, and magnesium when present separately. Strontium has also been determined simultaneously with sodium, potassium, calcium, and magnesium with a multi-channel photometer [354] and its determination in sea water [355] and in cement [356] has also been reported. Flame photometry has been used for the determination of trace metals in wine [357] and for the determination of inorganic sulphate [358] in serum after precipitation of this anion with an excess of barium chloride.

Absorptiometry.

Inorganic.—The development of absorptiometric methods during 1954 has been reviewed.[359] During 1955 many methods were reported in the literature, but few of these can be regarded as outstanding contributions.

Mehler [360] has reviewed potential errors in spectrophotometry with optically dense solutions, stressing the need for a truly monochromatic light source. The principles of precision colorimetry have been discussed, and it has been shown how variations in slit width, sensitivity, and dark current setting affect precision. Two new photometric procedures were proposed, which offer a possible increase in precision, but require more time and effort than normal methods.[361]

Copper has been determined photometrically with several reagents: tetraethylthiuram disulphide [34] which forms a yellow-brown copper complex in acid solution; sodium di-2-hydroxyethyldithiocarbamate [362] which is said to possess many advantages over sodium diethyldithiocarbamate; ethylenediaminetetra-acetic acid [363] and nitrilotriacetic acid; [364] 8-hydroxy- and 8-hydroxy-2-methyl-quinoline,[365] the latter being more suitable;

[347] P. Porter and G. Wyld, *Analyt. Chem.*, 1955, **27**, 733.

[348] R. F. Milton and W. D. Duffield, *Chem. and Ind.*, 1955, 280.

[349] R. Ishida, *J. Chem. Soc. Japan*, 1955, **76**, 56.

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[356] J. J. Diamond, *ibid.*, p. 913.

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[359] Anon., *Chemical Age*, 1955, **71**, 527.

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[363] W. Nielsch and G. Boltz, *Z. analyt. Chem.*, 1954, **143**, 1.

[364] *Idem, ibid.*, 1954, **142**, 406.

[365] J. Bernal-Nievas and L. Serrango Berges, *Anales Fis. Quim.*, 1954, *B*, **50**, 459.

guaiacol in ammonia solution;[366] hydrobromic acid (which cannot be used in the presence of iron);[367] diquinolol[368, 369] and sodium diethyldithiocarbamate.[370–372] Uranium has been determined by use of 1 : 3-dipentylpropanedi-1 : 3-one,[373] ammonium thioglycollate,[374] dibenzoylmethane[375, 376] (using ethyl acetate extraction), and by the thiocyanate method with[377] and without[378] extraction. Iron has been determined by using various reagents: ethylenediaminetetra-acetic acid,[379, 380] tartaric acid[381] in the presence of a periodate stabiliser, salicylaldehyde-glycinehydroxamic acid[382] over the pH intervals 2·35—3·34 or 5·06—10·26, phenazone–thiocyanate, the pink complex being extracted with amyl acetate at pH 2·5,[383] cupferron (methanol or butane-2 : 3-diol being used to keep the complex in solution),[384] dimethylglyoxime[385] but with use of pyridine rather than ammonia, with or without extraction by chloroform,[386] *o*-phenanthroline,[387, 388] and dipyridyl[389] and with sulphosalicylic acid[390] and variations of the thiocyanate method.[391–393]

Bismuth has been determined colorimetrically by use of thiourea,[394–396] hydrobromic acid,[397] sodium diethyldithiocarbamate,[398] and phenazone–potassium iodide.[399] Manganese has been determined by using sodium diethyldithiocarbamate,[400] the intense colour of the permanganate ion,[401] or that of the manganic ion following oxidation by bromate in 8N-nitric acid.[402] Ethylenediaminetetra-acetic acid[403] and dimethylglyoxime have

[366] M. Ya. Shapiro and V. G. Lupina, *Vinodelie i Vinogradstvo S.S.S.R.*, 1953, 6.
[367] W. Nielsch and G. Boltz, *Z. analyt. Chem.*, 1954, **142**, 427.
[368] L. Ghyssaert, *Bull. Cent. Belge Étud. Docum. Eaux*, 1954, 56.
[369] H. Jerome and H. Schmitt, *Bull. Soc. Chim. biol.*, 1954, **36**, 1343.
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[381] W. Nielsch and G. Böltz, *Metall*, 1954, **8**, 374.
[382] A. Mukherjee, *Naturwiss.*, 1955, **42**, 127.
[383] E. Sudo, *J. Chem. Soc. Japan*, 1954, **75**, 968.
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[385] N. Oi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75**, 1067.
[386] *Idem, ibid.*, p. 1069.
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[393] M. Gral-Cabanac, *Analyt. Chim. Acta*, 1955, **12**, 50.
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[396] W. Nielsch and G. Böltz, *Z. analyt. Chem.*, 1954, **143**, 168.
[397] *Idem, Analyt. Chim. Acta*, 1954, **11**, 438.
[398] K. L. Cheng, R. H. Bray, and S. W. Melsted, *Analyt. Chem.*, 1955, **27**, 24.
[399] E. Sudo, *J. Chem. Soc. Japan*, 1954, **75**, 1291.
[400] E. Specker, H. Hartkamp, and M. Kuchtner, *Z. analyt. Chem.*, 1954, **143**, 425.
[401] A. Kozawa, M. Tanaka, and K. Sasaki, *Bull. Chem. Soc. Japan*, 1954, **27**, 345.
[402] W. C. Purdy and D. N. Hume, *Analyt. Chem.*, 1955, **27**, 256.
[403] W. Nielsch and G. Böltz, *Analyt. Chim. Acta*, 1954, **11**, 367.

been used in the determination of nickel,[404, 405] and the former also for that of cobalt.[406] Other workers have used the terpyridyl,[407] nitroso-R-salt,[408] and thiocyanate [409] methods. Eriochrome-black T,[410] murexide,[411] bromoanilic acid,[33] and pyrazole-blue [412] have been used for the colorimetric determination of calcium, in addition to the alizarin [413] method. Barium has been determined in the presence of equal amounts of calcium and strontium by precipitation with ammonium molybdate [414] and subsequent determination of the molybdenum by the thiocyanate procedure. The latter procedure has been employed by some authors for the determination of molybdenum itself [415, 416] but others prefer to use the dithiol [417] procedure or the colour of the molybdoferrocyanide complex.[418] Two papers have reported on the tungsten thiocyanate method.[419, 420] Vanadium has been determined: by reduction to the quadrivalent state, reaction with ferric chloride and formation of colour of the ferrous iron thus produced with dimethylglyoxime,[421] by a catalytic effect based on the enhanced oxidation of aniline in the presence of complex-forming oxalate ions,[422] through the acceleration by vanadium of the oxidation of aniline by chlorates activated with 8-hydroxyquinoline,[423] by the colour produced with catechol [424] and also with molybdophosphate or tungstophosphate.[425] Ethylenediaminetetra-acetic acid [426] and diphenylcarbazide [427] have been used as reagents for the absorptiometric determination of chromium. The stereotyped rhodamine-B [428, 429] and thiourea [430] methods have been used for the determination of antimony, whilst arsenic has been determined turbidimetrically after reduction to elementary arsenic by hypophosphorus acid [431] or by the use of silver diethyldithiocarbamate after evolution as arsine.[432] Thiourea [433–436]

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has been used extensively in the absorptiometric determination of tellurium, and phosphorous acid has been employed to reduce it to metallic tellurium[437] before measurement of the absorption in the ultraviolet region. 3 : 3′-Diaminobenzidine yields an intense yellow piazselenol with selenite solutions; this has been used in the determination of selenium.[438] The structure of the aluminium–morin complex has been examined, and what is claimed to be a new method has been proposed on this basis.[439] In the aluminon method, precipitation of the aluminium lake has been prevented by formation of the aluminon–aluminium–sulphosalicylic acid complex.[440] Others[441] prefer Eriochrome-cyanine to aluminon. Ferroin[442] and the fluorescence of aluminium–8-hydroxyquinoline[443] under carefully controlled conditions have also been employed in absorptiometric methods for aluminium. Various reagents have been used in the absorptiometric determination of titanium: salicylhydroxamic acid[444] (yellow colour in dilute acid solution), " Tiron " in the presence of E.D.T.A.,[445] sulphosalicylic acid,[446] hydrogen peroxide,[447, 448] and thiocyanate.[449] Many authors report on variations of the silicomolybdate procedure for the determination of silicate in various materials.[450–456] 8-Hydroxyquinoline has been used for the direct colorimetric determination of magnesium[457] and also indirectly after treatment with sulphanilic acid and sodium nitrite.[458, 459] Titan-yellow[460] and Eriochrome blue-black B[461] have also been used as colorimetric reagents for determination of the same metal. The variables in the thiourea method for tin have been closely examined.[462] The tetrabromochrysazin[463] and dianthrimide[464] methods for boron have been re-investigated.

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[438] J. Hoste and J. Gillis, *Analyt. Chim. Acta*, 1955, **12**, 158.

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[459] M. Suzuki, *ibid.*, p. 93.

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[462] W. Nielsch and G. Böltz, *Z. analyt. Chem.*, 1954, **143**, 161.

[463] J. H. Yoe and R. L. Grob, *Analyt. Chem.*, 1954, **26**, 1465.

[464] H. Baron, *Z. analyt. Chem.*, 1954, **143**, 339.

Dithizone methods for silver,[465, 466] zinc,[467] cadmium,[468] and mercury [469] have been employed. Carmine-red [38] and quinalizarin [470] have been used for thorium, and *p*-phenetidine [471] and starch–iodine [472] (oxidation of potassium iodide) for thallium. Hydrogen peroxide,[473] 8-hydroxyquinoline,[474] and thiocyanate–acetone methods [475] have been used to determine niobium, and in the last case, tantalum was determined simultaneously by a modified pyrogallol procedure.

Cerium has been determined absorptiometrically with veratrole,[476] germanium with diphenylcarbazone,[477] gallium with rhodamine-B,[478] zirconium with alizarin-S,[479] beryllium by a new method with Solochrome brilliant-blue,[32] phosphorus by the molybdenum-blue method using ascorbic acid as reductant,[480] sodium by direct colorimetry with violuric acid in anhydrous dimethylformamide [481] and indirectly *via* uranyl thiocyanate following precipitation of sodium zinc uranyl acetate in the usual way,[482] the rare earths by aluminon [483] and alizarin-red S,[484] platinum by *p*-nitrosodimethylaniline,[485] and palladium by the same reagent or with ethylenediaminetetra-acetic acid,[486] β-nitroso-α-naphthol,[487] or thiourea.[488]

Hydrogen peroxide has been determined by addition of ferrous iron and thiocyanate,[489] and carbonyl sulphide by hydrolysis to sulphide and determination by the methylene-blue method.[490] Atmospheric sulphur dioxide [491] has been determined by catalytic reduction to hydrogen sulphide and reaction of the latter with ammonium molybdate, and sulphate [492] has been determined following conversion into sulphuric acid on a cation exchanger by treatment with lanthanum and a measured amount of solid thorium borate–amaranth reagent (the released dye is measured at 521 mμ). Nitrogen has been determined in steel by the ammonia–pyrazolone–pyridine method,[493] and in organic compounds following Kjeldahl digestion by reaction

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[466] M. Shima, *Jap. Analyst*, 1953, **2**, 96.
[467] T. Kato and S. Takei, *ibid.*, p. 208.
[468] A. Petzold and I. Lange, *Z. analyt. Chem.*, 1955, **146**, 1.
[469] A. C. Rolfe, F. R. Russel, and N. T. Wilkinson, *Analyst*, 1955, **80**, 523.
[470] A. Purushottam, *Z. analyt. Chem.*, 1955, **146**, 245.
[471] S. Iijima and Y. Kamemoto, *J. Chem. Soc. Japan*, 1954, **75**, 1294.
[472] V. S. Fikhengol'ts and N. P. Kozlova, *Zavodskaya Lab.*, 1955, **21**, 407.
[473] R. Pickup, *Colon. Geol. Min. Resources*, 1955, **5**, 174.
[474] J. L. Kassner, A. G. Paratla, and E. L. Grove, *Analyt. Chem.*, 1955, **27**, 492.
[475] A. E. O. Marzys, *Analyst*, 1955, **80**, 194.
[476] H. N. Antoniades, *Chemist-Analyst*, 1955, **44**, 34.
[477] G. S. Desmuk, *Zhur. analit. Khim.*, 1955, **10**, 61.
[478] H. Onishi, *Analyt. Chem.*, 1955, **27**, 832.
[479] E. C. Mills and S. E. Herman, *Metallurgia*, 1955, **51**, 157.
[480] L. Erdey, V. Felps, and E. Bodor, *Acta Chim Acad. Sci. Hung.*, 1954, **5**, 65.
[481] R. F. Muraca and J. P. Bonsack, *Chemist-Analyst*, 1955, **44**, 38.
[482] P. N. Kovalenko and V. V. Tenkovtsev, *Ukrain. khim. Zhur.*, 1954, **20**, 411.
[483] L. Holleck, D. Eckardt, and L. Hartinger, *Z. analyt. Chem.*, 1955, **146**, 103.
[484] R. W. Rinehart, *Analyt. Chem.*, 1954, **26**, 1820.
[485] J. J. Kirkland, *Diss. Abs.*, 1954, **14**, 760.
[486] W. M. MacNevin and O. H. Kriege, *Analyt. Chem.*, 1954, **26**, 1768.
[487] K. L. Cheng, *ibid.*, p. 1894.
[488] W. Nielsch, *Mikrochim. Acta*, 1954, 532.
[489] F. Patty and P. B. Maury, *Compt. rend.*, 1954, **239**, 976.
[490] L. A. Pursglove and H. W. Wainwright, *Analyt. Chem.*, 1954, **26**, 1835.
[491] H. Stratmann, *Mikrochem. Acta*, 1954, 668.
[492] J. L. Lambert, S. K. Yasuda, and M. P. Grotheer, *Analyt. Chem.*, 1955, **27**, 800.
[493] J. B. Lear, *Diss. Abs.*, 1954, **14**, 1520.

with phenol and hypochlorite in the presence of a nitroprusside catalyst.[494] Nitrite has been determined by reaction with thioglycollic acid and extraction with di*iso*propyl ether–pentanol–acetone.[495]

Chloride has been determined by reaction with silver iodate and liberation of iodine from the displaced iodate ion by treatment with acid and cadmium iodide–starch reagent.[496] The liberation of red Chromotrope-2B from the blue thorium lake by the fluoride ion has been used as a means of determining the latter.[497] It has also been determined after distillation of fluorosilicic acid by the bleaching of the thorium–alizarin lake.[498] Pyrophosphate has been determined by the cysteine-catalysed reaction with Fiske's molybdate reagent.[499] Hypophosphite has been determined by reaction with molybdic acid.[500]

T. S. W.

Radiochemical Methods of Analysis.

Radiochemical analysis was very briefly reviewed in *Annual Reports* for 1953,[501] but the importance of isotopic methods is now such that a special section is devoted to them. Radioactive and enriched stable isotopes are now generally available [502] and there are facilities for irradiating materials in high fluxes of thermal neutrons; [502] many laboratories are equipped to undertake isotopic work. Unless special problems are being studied, the assay of radioactive isotopes requires only apparatus which is available commercially; a list of equipment manufactured in Great Britain has been published.[503] The total cost of fitting a laboratory for simple radiochemical work compares favourably with the initial costs for other modern instrumental methods. For work with stable isotopes, a mass spectrometer is generally needed; commercial instruments are of necessity expensive but of course can be used for analytical purposes besides those involving isotopes.

There are now many useful text-books dealing with isotopic methods in Chemistry; there has been a series of ten articles [504] dealing with all aspects of work with radioactive isotopes. The Atomic Energy Authority of Great Britain has a school in which instruction in the uses of isotopes is given.

Two conferences, in 1951 and 1954, on the uses of radioactive isotopes have been organised by the Atomic Energy Research Establishment and held at Oxford. At both conferences, there was a very wide range of subjects since the only feature common to all the papers presented was the use of radioactive isotopes. The papers and the discussions on them have

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[494] B. Lubochinsky and J. P. Zalta, *Bull. Soc. Chim. biol.*, 1954, **36**, 1363.

[495] M. Ziegler and O. Glemser. *Z. analyt. Chem.*, 1955, **144**, 187.

[496] J. L. Lambert and S. K. Yasuda, *Analyt. Chem.*, 1955, **27**, 444.

[497] H. F. Liddell, *Analyst*, 1954, **79**, 752.

[498] L. Bloch, *Chem. Weekblad*, 1955, **51**, 65.

[499] R. M. Flynn, M. E. Jones, and F. Lipmann, *J. Biol. Chem.*, 1954, **211**, 791.

[500] G. Gutzeit, U.S.P. 2,697,651, 1954.

[501] C. L. Wilson, *Ann. Reports*, 1953, **50**, 375.

[502] " Radio-active Materials and Stable Isotopes," Atomic Energy Research Establishment, Harwell, 1954.

[503] " Radio Isotope Instrumentation and Accessories," edited by D. Taylor and A. G. Peacock, Scientific Instrument Manufacturers' Association of Great Britain, London, 1955.

[504] F. P. W. Winteringham, *Lab. Practice*, 1955, **4**, 94, 148, 196, 244, 288, 328, 370, 411, 449, 493.

been published.[505-508] In the summer of 1955, a large conference on the peaceful uses of atomic energy was held at Geneva. A meeting at Edinburgh on the use of radioactive materials in biological assays has been reported.[509] It is evident that workers in the medical and biochemical fields have been readier to apply isotopic methods than workers in the physical fields, but the methods are now being used in investigations of many types, *e.g.*, in research in the paint industry.[510] An indication of the wide application of these methods is the fact that titles of papers now do not always indicate that isotopic methods have been used in the work described.

The most significant point in connection with the use of radioactive isotopes in analysis is the great sensitivity of detection; depending upon the isotope being studied, the limit of detection is between 10^{-11} and 10^{-15} g.[511] Other important features of certain isotopic methods in analysis is their specificity, and the fact that the decay of a radioactive isotope is independent of its chemical and physical state.

Almost all the chemical applications of radioactive isotopes are analytical in nature. The topics discussed and the references cited in this Report have been selected to show the wide range of problems which can be tackled by isotopic methods; it has been necessary to choose those topics in which the analytical aspects of the work are stressed.

Isotopes as Accessories in Analysis.—The use of radioactive isotopes to determine the solubilities of sparingly soluble materials is well known; [512] labelled materials can also be used to study distribution equilibria, co-precipitation, adsorption, and other phenomena of importance in analytical procedures.

Efficiencies of separation can be assessed by labelling one of the components of a mixture and measuring activities during the course of the separation; the measurements can be rapid, non-destructive, and very sensitive. Radioactive isotopes have been used to test the separation by liquid–liquid extraction of the following pairs of elements: niobium and tantalum,[513] cobalt and zinc,[514] and protactinium and niobium.[515] The controlled-potential electro-separation of copper, bismuth, and lead has been tested [516] with radioactive isotopes. Isotopic methods have been employed [517] in a study of the purification of metals by zone melting. The separation of tin, antimony, and tellurium with anion-exchange resins,[518] and paper chromatographic methods for separating inorganic ions [519] and

[505] " Radio Isotope Techniques, Vol. I, Medical and Physiological Applications," H.M.S.O., London, 1953.

[506] " Radio Isotope Techniques, Vol. II, Industrial and Allied Research Applications," H.M.S.O., London, 1952.

[507] " Radio Isotope Conference, 1954, Vol. I, Medical and Physiological Applications," Butterworths, London, 1954.

[508] " Radio Isotope Conference, 1954, Vol. II, Physical Sciences and Industria Applications," Butterworths, London, 1954.

[509] R. F. Glascock, *Nature*, 1955, **176**, 427.

[510] D. F. Rushman, *J. Oil Colour Chemists' Assoc.*, 1953, **36**, 352.

[511] H. Seligman, ref. 506, p. 1.

[512] H. K. Zimmerman, *Chem. Rev.*, 1952, **51**, 25.

[513] J. Y. Ellenburg, G. W. Leddicotte, and F. L. Moore, *Analyt. Chem.*, 1954, **26**, 1045.

[514] H. A. Mahlman, G. W. Leddicotte, and F. L. Moore, *ibid.*, p. 1939.

[515] F. L. Moore, *ibid.*, 1955, **27**, 70.

[516] M. Ishibashi, T. Fujinaga, and Y. Kusaka, *J. Chem. Soc. Japan*, 1954, **75**, 13.

[517] P. Albert, F. Montariol, R. Reich, and G. Chaudron, ref. 508, p. 75.

[518] G. W. Smith and S. A. Reynolds, *Analyt. Chim. Acta*, 1955, **12**, 151.

[519] M. Lederer, *ibid.*, p. 146.

uranium from many metals [520] have been studied with radioactive isotopes. It has been shown [521] by labelling with ^{35}S that *cyclo*hexyl methyl sulphide can be completely separated from the corresponding sulphoxide by chromatography. Radioactive metallic tracers (in the form of salts) have been added to petroleums before ashing to see if the metals are completely retained in the ash.[522]

Isotopic methods have been used [523] to test precipitations in the colorimetric determinations of niobium and tantalum in steels. Procedures for the micro-determination of beryllium have been tested [524] with ^{7}Be. Methods for precipitating germanium have been examined [525] with ^{71}Ge. Radioactive isotopes have been used [526] in critical studies of methods for detecting and separating potassium, rubidium, and cæsium.

In very accurate absorptiometric determinations of niobium in minerals [527] and steels,[528] addition of ^{95}Nb at an early stage in the determination allows one to make corrections for small losses of the element during chemical separations. Isotopic methods have been combined with flame photometry to determine strontium in sea water,[529] and with *X*-ray spectrographic methods in analyses for uranium and thorium.[530]

^{60}Co has been used [531] for testing the various stages in the assay of vitamin B_{12}. Evaluations of determinations of iodine in biological materials have been carried out [532, 533] with ^{131}I. The removal from high polymers of materials of low molecular weight, *e.g.*, unused initiator, present at very low concentrations has been tested [534] with labelled materials. Efficiencies of fractionations of high polymers can readily be assessed [535] by using mixtures of unlabelled and labelled polymers.

Isotope Dilution Analysis.—A well-known and important application of radioactive isotopes and enriched stable isotopes is in the method of isotope dilution analysis.[536] This method is applied to the analysis of complex mixtures; it is essential that pure samples of the various components should be recovered from the mixture but the necessity for complete recovery is avoided. The calculations, when using radioactive labels, are simple; with stable labels the calculations are slightly more complicated because the concentration of the labelling atoms needs to be such that the molecular weight of the substance is affected.

In one method of working, the components of the mixture are unlabelled

[520] H. P. Raaen and P. F. Thomason, *Analyt. Chem.*, 1955, **27**, 936.
[521] G. Ayrey, D. Barnard, and C. G. Moore, *J.*, 1953, 3179.
[522] L. O. Morgan and S. E. Turner, *Analyt. Chem.*, 1951, **23**, 978.
[523] T. F. Boyd and M. Galan, *ibid.*, 1953, **25**, 1568.
[524] T. Y. Toribara and R. E. Sherman, *ibid.*, p. 1594.
[525] L. K. Bradacs, I.-M. Ladenbauer, and F. Hecht, *Mikrochim. Acta*, 1953, 229.
[526] W. Geilmann and W. Gebauhr, *Z. analyt. Chem.*, 1954, **142**, 241.
[527] G. W. C. Milner and A. A. Smales, *Analyst*, 1954, **79**, 315.
[528] *Idem*, *ibid.*, p. 425.
[529] A. A. Smales, *ibid.*, 1951, **76**, 348.
[530] W. J. Campbell and H. F. Carl, *Analyt. Chem.*, 1955, **27**, 1884.
[531] F. A. Bacher, A. E. Boley, and C. E. Shonk, *ibid.*, 1954, **26**, 1146.
[532] J. W. Decker and H. S. Hayden, *ibid.*, 1951, **23**, 798.
[533] H. Spitzy, *Mikrochim. Acta*, 1955, 130.
[534] J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Polymer Sci.*, 1954, **12**, 449.
[535] J. C. Bevington, G. M. Guzman, and H. W. Melville, *Proc. Roy. Soc.*, 1954, *A*, **221**, 437.
[536] See, *e.g.*, M. D. Kamen, "Radio Active Tracers in Biology," 2nd Edition, Academic Press, New York, 1951.

and it is necessary to prepare pure labelled samples of the components for which analyses are required. This method is likely to be encountered in analyses of commercial and natural products. Recent applications include analyses for substances of biological and biochemical interest, *e.g.*, penicillins,[537, 538, 539] vitamin B_{12},[540, 531] vitamin D,[541] 2:4-dichlorophenoxyacetic acid,[542] γ-hexachloro*cyclo*hexane,[543, 544] D- and L-glutamic acid,[545] D-glucose,[546] gentiobiose,[546] and thyroxine.[547] Other examples of isotope dilution analysis are the determinations of diethyl ether in mixtures of acrylic acid and ethanol,[548] triphosphates and pyrophosphates in mixtures,[549] zinc,[514, 550] lead,[551] niobium in mixed oxides of niobium, tantalum, and titanium,[552] water in solids,[553] and free sulphur in vulcanised rubber.[554]

Another method of working can be applied in research problems requiring the determination of the various products of a reaction; the products may be present in very small quantities. The reaction is performed with labelled reactants so that the products are labelled; unlabelled carriers are added. Purity of the isolated samples is extremely important since contamination by traces of a labelled impurity may seriously affect the results; the only conclusive test for efficiency of purification is to perform trials on a mixture of an unlabelled sample of the substance with labelled samples of all possible contaminants. Isotope dilution analysis of this type has recently been applied [555] to reactions involving substances of importance in radical polymerisations, *e.g.*, initiators, retarders, and inhibitors.

Isotope dilution analysis has been used by Grosse, Kirshenbaum, and their co-workers for the determination of oxygen in many compounds.[556] Molecular oxygen enriched in ^{18}O is added to the material and the conditions are adjusted so that there is complete exchange between the elementary oxygen and the oxygen in the specimen; comparison of the ^{18}O contents of the original oxygen and the equilibriated mixture allows calculation of the oxygen content of the specimen. In copper, oxygen contents between 0·01 and 0·1% by weight can be determined.[557] The method can also be used for other elements.

As a result of the development of mass-spectrometric techniques for solids and the availability of enriched isotopes for many elements, isotope

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[537] J. T. Craig, J. B. Tindall, and M. Senkus, *Analyt. Chem.*, 1951, **23**, 332.
[538] M. Gordon, A. J. Virgona, and P. Numerof, *ibid.*, 1954, **26**, 1208.
[539] G. C. Ashton and M. C. Foster, *Analyst*, 1955, **80**, 123.
[540] E. L. Smith, ref. 505, p. 281.
[541] P. Numerof, H. L. Sassaman, A. Rodgers, and A. E. Schaefer, *J. Nutrition*, 1955, **55**, 13.
[542] P. Sørensen, *Analyt. Chem.*, 1954, **26**, 1581.
[543] J. T. Craig, P. F. Tryon, and W. G. Brown, *ibid.*, 1953, **25**, 1661.
[544] R. Hill, A. G. Jones, and D. E. Palin, *Chem. and Ind.*, 1954, 162.
[545] C. C. Barker, I. W. Hughes, and G. T. Young, *J.*, 1951, 3047; 1952, 1574.
[546] J. C. Sowden and A. S. Spriggs, *J. Amer. Chem. Soc.*, 1954, **76**, 3539.
[547] E. P. Reineke, *J. Dairy Sci.*, 1954, **37**, 1227.
[548] J. G. Burtle and J. P. Ryan, *Analyt. Chem.*, 1955, **27**, 1215.
[549] O. T. Quimby, A. J. Mabis, and H. W. Lampe, *ibid.*, 1954, **26**, 661.
[550] K. Theurer and T. R. Sweet, *ibid.*, 1953, **25**, 119.
[551] H. von Buttlar, *Naturwiss.*, 1955, **42**, 90.
[552] J. Beydon and C. Fisher, *Analyt. Chim. Acta*, 1953, **8**, 538.
[553] R. Viallard and Marchetti, *Chim. analyt.*, 1954, **36**, 214.
[554] S. Ikeda and S. Kanbara, *J. Chem. Soc. Japan*, 1954, **75**, 1308.
[555] J. C. Bevington and H. W. Melville, ref. 508, p. 3.
[556] See, *e.g.*, A. D. Kirshenbaum and A. G. Streng, *Analyt. Chem.*, 1953, **25**, 638.
[557] A. D. Kirshenbaum and A. V. Grosse, *ibid.*, 1954, **26**, 1955.

dilution analysis can be applied to many solids. Thorium has been determined [558] in this way. Rocks have been dated [559] by determining the ratio of radioactive ^{87}Rb to stable ^{87}Sr. The use of the technique for trace impurities in solids has been discussed; [560] in many cases impurities at 10^{-10}% by weight can be detected.

The principle of isotope dilution is applied also in other analytical procedures involving isotopes.

Labelled Reagents.—In a number of cases an element or compound can be determined by reaction with a labelled reagent; the activity of a precipitate or a derivative can then be used to calculate the quantity of the element or compound in the sample. The method is capable of great sensitivity but it requires complete recovery of the pure derivative; this difficulty can be overcome in some cases by a double tracer technique.[561, 562] [^{131}I]*p*-Iodobenzenesulphonyl chloride ("pipsyl chloride") has been used as a reagent for amino-acids; [563] it is suitable for any amine which gives a crystalline pipsyl derivative. This reagent has been used in analyses for histamine [564] and pyrimidines,[565] and the double labelling technique has been used.[561, 562] Acetic anhydride labelled with ^{3}H and ^{14}C has been used as a reagent for hydroxy- and amino-compounds.[566] Compounds of these types have also been determined with 3-chloro-4-methoxybenzoyl chloride labelled with ^{36}Cl at the 3-position.[567] Amino-acids on paper chromatograms have been located with methyl [^{131}I]iodide followed by scanning of the paper for activity; [568] the reagent caused some methylation of the cellulose and a consequent increase in background. The positions of fatty acids on paper chromatograms may be fixed by converting the acids into their cobalt salts by use of ^{60}Co.[510]

The identification and estimation of the free radicals in reaction mixtures can be performed [569] by adding radioactive iodine to the system. The small amounts of the corresponding labelled iodides can then be determined by isotope dilution analysis.

Potassium has been determined with reagents labelled with ^{60}Co.[570-572] The same isotope has been used in reagents for the determination of thallium [573] and antimony.[574] [^{110}Ag]Silver nitrate has been used [575] in the

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[558] G. R. Tilton, L. T. Aldrich, and M. G. Inghram, *Analyt. Chem.*, 1954, **26**, 894.

[559] R. H. Tomlinson and A. K. Das Gupta, *Canad. J. Chem.*, 1953, **31**, 909.

[560] G. P. Barnard, *Analyst*, 1954, **79**, 594.

[561] A. S. Keston and J. Lospalluto, *Fed. Proc.*, 1951, **10**, 207.

[562] A. S. Keston, S. Undenfriend, and M. Levy, *J. Amer. Chem. Soc.*, 1947, **69**, 3151; 1950, **72**, 748.

[563] A. S. Keston, S. Undenfriend, and R. K. Cannan, *ibid.*, 1946, **68**, 1390; 1949, **71**, 249.

[564] R. W. Schayer, Y. Kobayashi, and R. L. Smiley, *J. Biol. Chem.*, 1955, **212**, 593.

[565] J. R. Fresco and R. C. Warner, *ibid.*, 1955, **215**, 751.

[566] P. Avivi, S. A. Simpson, J. F. Tait, and J. K. Whitehead, ref. 507, p. 313.

[567] P. Sørensen, *Analyt. Chem.*, 1955, **27**, 388.

[568] F. P. W. Winteringham, A. Harrison, and R. G. Bridges, ref. 505, p. 352.

[569] G. R. Martin, ref. 506, p. 115.

[570] E. Sanchez Serrano and I. Lopez Santos, *Bol. radiactividad*, 1951, **24**, 49.

[571] T. Ishimori and Y. Takashima, *Bull. Chem. Soc. Japan*, 1953, **26**, 481.

[572] I. M. Korenman, F. R. Sheyanova, and Z. I. Glazunova, *Zavodskaya Lab.*, 1955, **21**, 774.

[573] T. Ishimori, *Bull. Chem. Soc. Japan*, 1953, **26**, 336.

[574] T. Ishimori and K. Ueno, *ibid.*, 1955, **28**, 200.

[575] C. Barcia Goyanes, E. Sanchez Serrano, and C. Gamis, *Bol. radiactividad*, 1954, **26**, 37.

formation of Ag_2TlPO_4 and Ag_2TlAsO_4 and the determination of phosphates and arsenates. Quantitative paper chromatography with traces of metal ions has been achieved with the aid of hydrogen [^{35}S]sulphide.[576] The small amounts of silver in photographic images have been determined [577] by converting the silver into silver [^{131}I]iodide; the method could be adapted for the determination of small amounts of silver chloride, bromide, or sulphide. This procedure is similar to one proposed [578] earlier, *viz.*, the conversion of the silver into cobalt ferrocyanide by means of ^{60}Co.

Activation Analysis.—Neutron activation analysis is a powerful method for elementary analysis particularly suited for the determination of trace quantities; [579] with certain limitations, it is independent of the chemical nature of the material. The method depends upon the fact that the atoms of many elements are converted into radioactive isotopes by reactions with slow neutrons; other bombarding particles—α-particles, protons, and deuterons—can be used for activation, but activation by neutrons is generally favoured.[580]

The method was described in *Annual Reports* of 1949; [581] reviews published since 1949 include those by Smales [580] and Meinke.[582] Usually the very high fluxes of thermal neutrons available in nuclear reactors are used, but small neutron sources, *e.g.*, a 25-mg. radium–beryllium source, can be used successfully in many cases; [583] sources of this kind can be installed in almost any laboratory.

Usually it is necessary to add carriers to the irradiated samples and then, following the procedure of isotope dilution analysis, to isolate pure specimens and determine their activities. Recent developments have simplified the chemical manipulations. The activities due to the various isotopes in a mixture can be measured by using filters chosen so that they absorb the radiations emitted by certain of the isotopes. The filter technique is not generally applicable and results in some loss of sensitivity. γ-Spectrometry can be used for detecting and estimating γ-emitters in mixtures,[584–586] provided that the energies of the γ-photons are not too close together.

Some of the recent applications of the neutron activation technique have been concerned with trace impurities in semi-conductors. Analyses for arsenic in germanium dioxide,[587] copper in germanium,[588] phosphorus in silicon,[589] arsenic in silicon,[590] and various impurities in silicon [585] have been reported; a typical sensitivity is the determination of 3×10^{-4} μg. of arsenic in a 1-g. sample of silicon.

[576] P. C. van Erkelens, *Nature*, 1953, **172**, 357.

[577] A. E. Ballard, C. W. Zuehlke, and G. W. W. Stevens, ref. 506, p. 105.

[578] N. C. Baenziger, *J. Chem. Phys.*, 1948, **16**, 1175.

[579] W. A. Brooksbank, G. W. Leddicotte, and H. A. Mahlman, *J. Phys. Chem.*, 1953, **57**, 815.

[580] A. A. Smales, ref. 506, p. 162.

[581] *Idem, Ann. Reports*, 1949, **46**, 285.

[582] W. W. Meinke, *Science*, 1955, **121**, 177.

[583] W. W. Meinke and R. E. Anderson, *Analyt. Chem.*, 1953, **25**, 778.

[584] R. E. Connally and M. B. Leboeuf, *ibid.*, p. 1095.

[585] G. H. Morrison and J. F. Cosgrove, *ibid.*, 1955, **27**, 810.

[586] A. A. Smales and L. Salmon, *Analyst*, 1955, **80**, 37.

[587] A. A. Smales and B. D. Pate, *Analyt. Chem.*, 1952, **24**, 717.

[588] G. Szekely, *ibid.*, 1954, **26**, 1500.

[589] J. A. James and D. H. Richards, *Nature*, 1955, **176**, 1026.

[590] *Idem, ibid.*, 1955, **175**, 769.

The technique has been applied to the determination of very small quantities of impurities in aluminium,[591, 592] aluminium alloys,[593] magnesium,[594] and iron.[595] It has been suggested [596] that 5 × 10^{-7}% by weight of phosphorus in aluminium or aluminium oxide could be determined quite readily by this technique. The method is particularly suitable for analyses for impurities in aluminium since only a negligible activity is induced in the matrix by slow neutrons; with fast neutrons, however, the reaction $^{27}\text{Al}(n, \alpha)^{23}\text{Na}$ occurs and it can interfere with the determination of sodium in aluminium.

Neutron activation analysis has been used to determine sodium and potassium in mixtures. The method has been applied to single nerve fibres,[597, 598] in which the sodium content may be only 1 μg. and the potassium content not much greater; it was concluded that the method is about 20 times as sensitive as methods with the flame photometer. The technique has been applied to the dating of potassium minerals.[599] The rubidium and cæsium contents of sea water and related materials have been measured;[586] for sea water there was a preliminary concentration by means of a cation-exchange resin. The arsenic content of sea water can be measured directly by neutron activation.[600]

Activation analysis has been used [601] for mixtures of rare earths by using a small neutron source; in many cases the method is much superior to spectrophotometric methods. Other examples of recent applications of the technique are the determinations of antimony,[602] indium,[603] cerium,[604] tantalum,[528, 552, 605] and thorium.[606]

The analyses considered so far have depended upon the occurrence of (n, γ) reactions. With slow neutrons ^{235}U undergoes fission to give ^{140}Ba among many products, and the yield of ^{140}Ba is a measure of the ^{235}U content of the original material. Several papers on the determination of uranium by neutron activation have been published.[607-610] ^{6}Li readily undergoes a (n, α) reaction with slow neutrons; the tritium produced can be used to determine [611] the original ^{6}Li. This reaction is also used [612] in a determination of the oxygen content of powdered beryllium; the beryllium is

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[591] R. C. Plumb and R. H. Silverman, *Nucleonics*, 1954, **12** [12], 29.
[592] P. Albert, M. Caron, and G. Chaudron, ref. 506, p. 171.
[593] B. M. Thall and B. Chalmers, *J. Inst. Metals*, 1950, **77**, 79.
[594] G. J. Atchison and W. H. Beamer, *Analyt. Chem.*, 1952, **24**, 1812.
[595] P. Albert, M. Caron, and G. Chaudron, *Compt. rend.*, 1953, **236**, 1030.
[596] L. M. Foster and C. D. Gaitanis, *Analyt. Chem.*, 1955, **27**, 1342.
[597] P. R. Lewis, ref. 505, p. 381.
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mixed with 7 times its weight of lithium fluoride and irradiated. The reaction $^{6}Li(n, \alpha)^{3}H$ is followed by $^{16}O(t, n)^{18}F$. The fluorine isotope is radioactive with a half-life of 112 min.; it is finally precipitated as PbClF for assay. The oxygen content of the lithium fluoride may be significant in this analysis.

In some cases considerable care is needed in planning the analyses. The determination of arsenic in germanium [587] depends upon the reaction $^{75}As(n, \gamma)^{76}As$, but ^{75}As can also be produced from the matrix by the reactions $^{74}Ge(n, \gamma)^{75}Ge$ and $^{75}Ge \xrightarrow{\beta^-} {}^{75}As$. ^{76}As can also be formed from bromine and selenium by the reactions $^{79}Br(n, \alpha)^{76}As$ and $^{76}Se(n, p)^{76}As$, so these elements may interfere with the determination of arsenic. In the determination of phosphorus in silicon,[589] it must be noted that silicon can be converted into an isotope of phosphorus thus

$$^{30}Si(n, \gamma)^{31}Si \qquad {}^{31}Si \xrightarrow{\beta^-} {}^{31}P$$

and the phosphorus so produced can contribute to the apparent phosphorus content of the silicon. Analyses for sulphur and phosphorus in magnesium are complicated [594] if the specimen contains chlorine, because of the reactions $^{35}Cl(n, p)^{35}S$ and $^{35}Cl(n, \alpha)^{32}P$. In analyses for trace impurities, the possibility of the matrix's being converted into the impurity being studied must always be considered.

Neutron activation has been used [613] to follow the small changes in bromine content caused by chemical manipulation of brominated polystyrene. The technique has also been used in conjunction with paper chromatography. The bromine analogue of D.D.T. was located [568] on a chromatogram by exposing the paper to a neutron flux and scanning for ^{82}Br activity; similarly the α-, β-, γ-, and δ-isomers of hexachloro*cyclo*hexane were located [568] by means of the reaction $^{35}Cl(n, p)^{35}S$. In applications of these types difficulties may arise from losses of hydrogen [^{82}Br]bromide for example, from the unknown and standard, and these should be similar both chemically and physically.

Ordinarily in activation analysis it is necessary that radioactive isotopes of fairly long half-life should be produced, although a half-life of only 22 min. for ^{233}Th is sufficient to permit the determination [606] of thorium by this method. A development [614] in activation analysis is the irradiation together of the sample and a nuclear emulsion. The activities of short-lived isotopes may be detected by the emulsion. In addition, elements which undergo nuclear reactions but only to produce stable isotopes may also be determined, for example ^{10}B undergoes a (n, α) reaction readily and the α-particles can be detected by the emulsion; this has also been described by French authors.[615]

Photoneutron Methods.—The reaction $^{9}Be(\gamma, n)2^{4}He$ occurs with γ-rays more energetic than 1·63 mev, and has been utilised [616] in a sensitive method for determining beryllium. The emitted neutrons are moderated and then detected with ^{10}B-enriched boron trifluoride counters. A ^{124}Sb source is

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recommended; the precautions needed in using a 1-curie γ-source are considerable, but 1 p.p.m. of beryllium can be detected. The method is specific since no other element has a photoneutron threshold below 2·04 mev which corresponds to the most energetic γ-photons from ^{124}Sb; the presence of lithium, boron, or cadmium in the specimen is undesirable since these elements have large cross-sections for the capture of thermal neutrons.

A new method for deuterium analysis uses [617] the reaction $^{2}\text{D}(\gamma, n)^{1}\text{H}$. The threshold is 2·23 mev and ^{24}Na has been used as the γ-source. Beryllium is the only element which can interfere, but samples should have similar compositions so that moderation of the neutrons and absorption of the γ-rays are similar; otherwise the purity of the sample is not critical.

The reaction $^{16}\text{O}(\gamma, n)^{15}\text{O}$ forms the basis of a method [618] for determining oxygen in organic compounds and metals. It is necessary to use γ-rays of energies greater than 15·5 mev; the short-lived activity of ^{15}O is measured.

Another nuclear reaction involving the release of neutrons, *viz.*, $^{14}\text{N}(d, n)^{15}\text{O}$, has been used [619] for analytical purposes. The mass of nitrogen in a specimen is calculated from the observed ^{15}O activity and the deuteron flux; in metals, nitrogen contents as low as 1 p.p.m. have been measured.

Other Uses of Isotopes in Analysis.—The natural radioactivity of potassium, due to ^{40}K, has been used [620, 621] in methods for determining this element; an accuracy of 1% or better is possible.[510] The radiations from ^{87}Rb, a naturally occurring isotope, are less penetrating than those from ^{40}K, and the difference has been utilised [622] in a method for determining potassium and rubidium in mixtures.

The uses of labelled substances for analyses of high polymers have been summarised.[555] Accurate determinations of the amounts of initiators, retarders, and transfer agents incorporated in polymers during their preparation are possible; the technique is valuable for analyses of co-polymers in those cases where the compositions of the monomer units are very similar or when one component is present only in small proportions. It is also possible to study similarly reactions between high polymers and materials of low molecular weight, *e.g.*, the quantity of *p*-benzoquinone which becomes chemically incorporated with poly(methyl methacrylate) when mixtures of the quinone and the polymer are irradiated, has been found.[623]

The *X*-ray absorption method for determining traces of heavy elements in organic materials has been reviewed.[624] In some cases there are considerable advantages in using radioactive isotopes as the sources of γ- or *X*-rays for this purpose.[625] The isotope ^{55}Fe which emits *X*-rays because of *K*-capture, is regarded [626] as the most suitable for the determination of sulphur in hydrocarbons.

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A neutron-scattering method for determining soil moisture has been described.[627] It depends upon the fact that hydrogen atoms are particularly effective in slowing down neutrons. A source of fast neutrons and a detector for slow neutrons are required. The method actually determines the hydrogen content of the soil, but practically all the hydrogen in mineral soils is in the form of water.

The amount of β-radiation scattered from a sheet of material depends upon the atomic number of the scatterer. This fact forms the basis for a method for analysis of chromium–niobium alloys;[628] the amount of radiation scattered is compared with that scattered from standards. The method can be extended to other alloys provided that the atomic numbers of the components differ appreciably.

Other applications of radioactive isotopes which are of some significance in analysis are the use of isotopes for calibrating micro-calorimeters,[629, 630] the use of a radioactive falling-ball viscometer for opaque viscous liquids[631] and the use of β-sources for dispersing static electricity on films and powders.[632]

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[630] W. B. Mann, *J. Res. Nat. Bur. Stand.*, 1954, **52**, 177.

[631] J. Guéron, ref. 506, p. 6.

[632] See, *e.g.*, P. S. H. Henry, ref. 506, p. 150.