Microchemical

Systematic Semi-micro Procedure for the Qualitative Analysis of the Commoner Cations. J. H. Winkley, L. K. Yanowski and W. A. Hynes. (*Mikrochem.*, 1936, **21**, 102–116.)—A scheme of analysis is given for the following cations: silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, iron, chromium, aluminium, zinc, manganese, calcium, barium, strontium, magnesium, potassium, sodium, lithium and ammonium. Spot tests are used directly, and not merely as confirmatory tests, but not for the members of the alkaline earth and alkali groups. The solutions used contained sufficient amounts of the nitrates and chlorides to furnish concentrations of 10 mg. of the cations per ml. The maximum initial volume of solution employed in any analysis was never more than 0·2 ml.; the amount of any cation present in the solution never exceeded 2 mg. A complete list of the concentrations of test substances and reagent solutions is given. The reagents are those found to give best results with relatively inexperienced workers. J. W. M.

Micro-determination of Chloride in Biological Fluids with Solid Silver Iodate. J. Sendroy. (I) **Gasometric Analysis.** (*J. Biol. Chem.*, 1937, **120**, 335–403.)—Small amounts of chlorine in biological fluids may be determined by the following general procedure:—The sample is diluted in an acid solution (usually with 0·085 *M* phosphoric acid) to a *p*H between 2·0 and 3·0 and to a chloride concentration between 0·012 and 0·003 *M*. Solid silver iodate is then added, with vigorous shaking, which causes the precipitation of the chloride and the release of iodate into the solution. The precipitate of silver chloride and the excess of silver iodate are removed from the solution by centrifuging. The supernatant liquid is then analysed gasometrically for iodate by means of an alkaline hydrazine solution. For details of the method and for the calculation of the results, the original paper should be consulted.

(II) **Titrimetric Analysis.** (*Ibid.*, 405–417.)—The preparation of the sample is the same as that described above. An aliquot portion of the supernatant liquid, after centrifuging, is treated with potassium iodide, and the liberated iodine is titrated with 0·03 *N* sodium thiosulphate solution, starch paste being used as indicator. S. G. S.

Tests on Photographic Paper. I. M. Korenman. (*Mikrochem.*, 1936, **21**, 17–20.)—Glossy or semi-matt silver-bromide photographic paper is treated with 10 per cent. sodium thiosulphate to remove the silver salts, and well washed, after which the moist paper is immersed in one of the following reagent solutions and dried. *Solutions.*—(1) For the detection of ferric iron and copper: 10 per cent. solution of potassium ferrocyanide. (2) For the detection of nickel: saturated alcoholic solution of dimethyl glyoxime. (3) For the detection of stannous tin: 1 per cent. gold chloride solution; the test-paper is coloured pale yellow. (4) For the detection of sulphur: saturated solution of lead acetate. (5) For the detection of gold: dilute stannous chloride and pyrogallol solution. (6) For the detection of nitrite: Griess's reagent. *Method.*—A drop of the test solution (0·25 c.mm.) is placed on the reagent paper, where it makes a stain 1 to 1·5 mm. in diameter. When the correct ion is present, the stain rapidly takes on the colour of the reaction product. Although such very small amounts of substance are used, no microscope is necessary, as with reactions in threads. The limits of identification and concentration compared with those of the same test on filter-paper are given below; the reagent solutions are those given above:—

		On filter-paper		On photographic paper	
Ion	Reagent	Limit of identification	Concentration limit	Limit of identification	Concentration limit
$Fe^{\cdots}$ ..	1	1γ	1 : 20000	0·0008γ	1 : 300000
$Cu^{\cdot\cdot}$ ..	1	2γ	1 : 10000	0·0025γ	1 : 100000
$Ni^{\cdot\cdot}$ ..	2	0·025γ	1 : 800000	0·0003γ	1 : 800000
S'' ..	4	1·8γ	1 : 11000	0·005γ	1 : 50000
NO_2' ..	6	0·015γ	1 : 1300000	0·0002γ	1 : 1300000
		In threads			
$Sn^{\cdot\cdot}$ ..	3	0·003γ (cotton)	—	0·007γ	1 : 36000
$Au^{\cdots}$ ..	5	0·002γ (silk)	—	0·016γ	1 : 15600

The nitrite test may be applied to detect nitrous oxide in the atmosphere; as little as 0·2γ per litre may be detected. J. W. M.

Micro-determination of Blood Sugar by Ceric Sulphate Titration. G. Giragossintz, C. Davidson and P. L. Kirk. (*Mikrochem.*, 1936, **21**, 21–34.)—Ferricyanide in alkaline solution is used to oxidise the sugar, and the resulting ferrocyanide is titrated in acid solution with standard ceric sulphate, alphazurine G.G. or phenanthroline ferrous complex being used as indicator. The excess of ferricyanide has no influence on the results and the titration of the ferrocyanide proceeds smoothly to a sharp and reproducible end-point. *Reagent Solutions.*—14 per cent. sodium carbonate solution, made from the anhydrous salt; 3–5 *M* sulphuric acid solution; 0·8 per cent. potassium ferricyanide solution. Standard ceric sulphate solution, preferably about 0·0025 *N*, prepared by the method of Willard and Young (*J. Amer. Chem. Soc.*, 1929, **51**, 149). It is standardised against a weighed sample of potassium ferrocyanide which has been recrystallised and dried. Standard ceric sulphate solution must be kept in a glass bottle, free from organic contamination. *Indicator.*—Either 0·4 per cent. Alphazurine G.G., or 0·025 *M* phenanthroline ferrous complex. *Method.*—The blood is deproteinised

in the usual way. Either 2 ml. of the blood filtrate which has been diluted to 1 : 10, or 1 ml. if the dilution was 1 : 5, is pipetted into a large test-tube. To this are added 2 ml. of the ferricyanide solution and 2 ml. of the sodium carbonate solution. A blank solution is also prepared with distilled water in place of the blood filtrate. The tubes are shaken, heated for about 5 minutes on the water-bath, and then cooled, 2 ml. of sulphuric acid are added, followed by a drop of indicator, and the solutions are titrated with the standard ceric sulphate to the end-point, which is a sharp change from yellow to brown with Alphazurine G.G., or from orange to green with phenanthroline. A 10-ml. burette calibrated in divisions of 0·02 ml. is convenient for the titration when 0·0025 *N* ceric sulphate solution is used. Over the entire range investigated, the same factor holds good, *viz.* 1 mg. of glucose ≡ 2·735 ml. of 0·01 *N* ceric sulphate solution. The method has been tested in comparison with other methods, and is claimed to be simpler, more readily reproducible and more rapid than those tried, and to give the same value for glucose. J. W. M.

Differentiation of Chromate and Dichromate Ions. M. G. Malko, L. K. Yanowski and W. A. Hynes. (*Mikrochem.*, 1936, **21**, 57–60.)—Hexamminocobaltic chloride will distinguish between chromate and dichromate ions microscopically in the absence of interfering ions, such as metavanadate, ferrocyanide, ferricyanide, tungstate, molybdate, tetrathionate, ortho- and pyro-phosphate ions. The reagent is a solution of the salt containing 28 g. per litre. Precipitation is carried out at room temperature by mixing one drop of the test solution with two drops of reagent on a slide. With the chromate ion alone, lemon-yellow needles are formed which attain the size of 1 cm. or more, whilst with the dichromate ion the crystals are orange-yellow and microscopic in size, showing a tree-like branching of prisms from a common stalk. Neither crystals resemble those formed on evaporating the reagent. The formula of the chromate precipitate is $(Co[NH_3]_6)(CrO_4)Cl$, and that of the dichromate compound $(Co[NH_3]_6)_2(Cr_2O_7)_3$. On recrystallisation the chlorochromate gives long golden-yellow needles, the dichromate light yellow six-sided or square platelets. With mixtures of chromate and dichromate ions there is a tendency for the precipitation to be retarded and for the chromate needles to be shorter. The proportion limits of the detection of the anions in the presence of each other is $20Cr_2O_7 : 1CrO_4$ and $2{\cdot}5CrO_4 : 1Cr_2O_7$. Two photomicrographs and 4 drawings are given. J. W. M.

Use of Complex Salts for the Detection of Anions. I. Hexamminocobaltic Chloride. W. A. Hynes and L. K. Yanowski. (*Mikrochem.*, 1937, **23**, 1–9.)—By the use of the reagent and procedure described in the preceding abstract the following ions were found to give characteristic crystalline reaction products when treated with hexammino-cobaltic chloride: bifluoride, bisulphate, bisulphite, chromate, cobaltinitrite, dichromate, dithionate, ferricyanide, ferrocyanide, fluosilicate, iodate, iodide, metavanadate, nitroprusside, orthovanadate, permanganate, persulphate, phosphomolybdate, phosphotungstate, pyrophosphate, sulphate, sulphosalicylate, tartrate, tellurite and thiosulphate. Of these, the following were found to give rapid qualitative tests: bisulphite, chromate, dichromate, dithionate, ferricyanide, ferrocyanide, iodate, permanganate, sulphate,

sulphosalicylate and thiosulphate. The cation present in the test substance apparently causes no difference in the crystalline form of the reaction product obtained. The anions react in much the same manner on treatment with the reagent, regardless of whether they are in the form of their salts or occur in solutions containing several anions. Twenty-four photomicrographs are given. J. W. M.

Colorimetric Micro-determination of Manganese. C. P. Sideris. (*Ind. Eng. Chem., Anal. Ed.*, **1937**, **9**, 445–446.)—Small amounts of manganese (1 to 20γ in 10 ml.) may be determined by the formaldoxime reagent of Denigès (*Compt. rend.*, **1932**, **194**, 895). The reagent is prepared by dissolving 20 g. of trioxymethylene and 47 g. of hydroxylamine sulphate in 100 ml. of water, by heating. To the slightly acid manganese solution (10 ml.) about 5 drops of 40 per cent. potassium hydroxide solution and 3 drops of the formaldoxime reagent (*cf.* ANALYST, **1934**, **59**, 200) are added. A wine-red colour immediately develops, and may be compared colorimetrically with that given by a standard manganese solution treated similarly. The amount of manganese in the unknown and standard solutions should be closely similar for accurate results. The addition of a suitable colloid (0·5 ml. of a 5 per cent. solution of gum Ghatti) to the solution prior to the development of the colour is advantageous. Ferric iron, even in traces, interferes by producing a similar red colour. This colour may be prevented from forming by the addition of 0·5 ml. of 20 per cent. sodium cyanide solution to the liquid before adding the formaldoxime. This results, however, in a greenish-yellow colour being formed by the iron, which also interferes, but to a lesser degree. It is necessary, therefore, that the amount of iron present in association with the manganese be determined and added in equal amount to the standard comparison solution. S. G. C.