

Rapid Test for Chlorate. H. R. Offord. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 93-95.)—A test-paper method has been devised for testing for chlorate in a few drops of solution. *Test-paper.*—No. 1 Whatman paper is soaked in 3 *N* ammonium thiocyanate solution and dried in a current of warm air at a temperature not exceeding 70° C. The dry paper may be kept without deterioration for several months if protected from light and dust. *Method.*—A drop of the solution to be tested is added to the paper, which has been dried before use at 60° C. for 10 minutes. The paper is supported on glass and placed in a drying oven at 95 to 105° C. for 5 to 30 minutes, the time required being the longer with small amounts of chlorate. A yellow colour is produced when chlorate is present. The use of duplicate test-papers is advised. The smallest detectable concentration of chlorate (either the sodium, potassium or calcium salt) was found to be 0.01 mg. per ml. The colour produced varies from a pale lemon-yellow (0.01 to 1.0 mg. per ml.), through a lemon-chrome (1 to 10 mg. per ml.), to orange or cadmium-yellow (over 10 mg. per ml.). The yellow colour is chiefly due to canarine ($C_8H_8N_8OS_7$) and pseudothiocyanic acid ($C_3HN_3S_3$). Chlorate in concentration of 0.1 mg. per ml. can be detected when present in 0.1 *N* solutions of sulphuric, nitric, acetic and oxalic acids, or sodium hydroxide, and also in acid or alkaline solutions containing 100 mg. per ml. of sodium chloride. Cyanide, thiosulphate and sulphite tend to interfere when present in quantity greater than the chlorate. The presence of any appreciable quantity of iron masks the test, and halogens, bromate, iodate, hypohalites, persulphate, peroxide (but not perborate) and cupric salts yield colours similar to that given by chlorate. *Application to plant extracts.*—Among tests carried out, it was found that chlorate in concentration of 0.05 mg. per ml. added to *Nitella* expressed sap was readily detected, the pale yellow colour of the sap itself not interfering. Positive results for chlorate were obtained in unfiltered or unclarified cold-water extracts of 1-g. samples of roots, stem, leaves and petioles of *R. petiolare*, when the plants had previously been soaked in dilute sodium chlorate solution, extracts of the untreated plants giving no interfering colour.

S. G. C.

Detection of Small Quantities of Perchlorates. D. Krüger and E. Tschirch. (*Z. anal. Chem.*, 1931, 85, 171-176.)—Monnier's methylene blue test for perchlorates (*ANALYST*, 1917, 42, 51) is applied on the micro-scale, and details of the sensitiveness of the test in different conditions are investigated. On the macro-scale, using 1 c.c. of test solution in a test tube, the smallest amount of perchloric (ClO_4) ion detectable is 1000 γ , and the limit of dilution 1 : 1000. For the micro-test one drop of the solution under examination is evaporated to dryness

on a slide, and one drop of a 0.2 per cent. aqueous solution of methylene blue is added. Blue and blue violet, needle-shaped crystals and crystal aggregates are formed in the presence of perchlorates, and may be seen under the microscope. The smallest amount recognisable is 3 γ of ClO_4 , and the limit of dilution is 1 : 17000; sulphate and acetate ions do not interfere. The test is more sensitive in a saturated solution of sodium acetate, when 0.5 γ of ClO_4 is detectable in a 1 : 100,000 dilution. In the presence of cellulose acetate 2.5 γ of ClO_4 is detectable in a dilution of 1 : 20,000. The test has been applied in an investigation of the use of perchloric acid as a catalyst in acetylations of cellulose. When sulphuric acid is used as a catalyst the cellulose acetate contains some sulphate in the form of ester, but when perchloric acid is used the perchlorate contamination in the cellulose acetate is undetectable by the methylene blue method, and is therefore less than 0.01 per cent.

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Use of Methylene Blue as a Reagent in Chemical Analysis. Application of the Process to the Detection and Estimation of Perchlorates in Chile Saltpetre. A. Monnier. (*Arch. Sci. phys. nat.*, 1916, [iv.], 42, 210-216; through *J. Chem. Soc.*, 1916, [ii.], 110, 639-640.)—The following acids in dilute solutions, preferably in the form of their alkali salts, give coloured, crystalline precipitates with a solution of methylene blue. Hydriodic acid gives a deep blue precipitate, showing bronze-green by reflection; perchloric and hydroferricyanic acids, violet precipitates, bronze-green by reflection; persulphuric, dichromic, and permanganic acids, rose-violet precipitates, bronze-green by reflection; metavanadic, molybdic, and tungstic acids, deep blue precipitates. The precipitate with a persulphate is readily distinguished from that with a perchlorate in that the former when calcined leaves a slight residue showing the reactions of a sulphate, and the latter when heated decomposes violently with deflagration. The amount of potassium perchlorate can be readily estimated colorimetrically in a sample of Chile saltpetre by this method. To 20 c.c. of a 5 per cent. solution of the crude nitrate 1 c.c. of a 0.3 per cent. solution of methylene blue in water is added, and the mixture left overnight. A crystalline precipitate forms, and the supernatant liquid is tinted blue. This colour is compared with that of standard tubes containing varying amounts of pure potassium perchlorate. If the perchlorate is present to the extent of less than 0.2 per cent., a 10 per cent. solution of crude nitrate, and if more than 0.5 per cent., a 2.5 per cent. solution of crude nitrate, is used. If the crude nitrate contains any iodide, this can be first removed by shaking the solution with moist silver oxide.