NOTES.

Pregl's Universal Filling applied to Macro-combustions. By WILLIAM DAVIES.

THE filling used in Pregl's method (" Die Quantitative Organische Mikroanalyse," 1923) of carbon and hydrogen determination has now been applied successfully on a macro-scale, and as such a universal filling has many advantages, the method is briefly indicated.

An ordinary combustion tube of about 1·2—1·5 cm. internal diameter and 95—100 cm. long is used. A plug of silver wool or silver gauze (1·5 cm.) precedes the filling of mixed copper oxide (wire form) and lead chromate (about 43 cm.); this is followed by a mixed silver wool and asbestos plug (2·5 cm.), and finally by a filling of lead peroxide asbestos (about 13 cm.). The last is prepared after Pregl (*op. cit.*, p. 29), but the thorough drying of this material on a large scale offers some difficulties, for the temperature at which the peroxide begins to decompose is somewhat uncertain (100—290°; see Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VII, p. 687); that used in these experiments was dried in bulk at 200° for 4 hours, then spread out in shallow vessels and dried for 8 hours over calcium chloride at 100° under less than 30 mm. pressure, and finally heated before use for 3 hours in a rapid stream of air in the combustion tube at 180°. Even after this treatment a trace of moisture was still left, and the first value for hydrogen with a new tube was apt to be slightly high. The lead peroxide in the combustion tube is heated by a hollow boiler (15 cm. long and with a hole of 2·5 cm. diameter) made of brazed copper and is modelled on Pregl's "Hohlgranate." The "Kupferbügel" is best in the form of an almost cylindrical piece of copper (5 cm. long) which practically surrounds the combustion tube and is connected round the middle to the copper boiler by means of a thick copper rod. The boiler requires about 50 c.c. of liquid, and technical *o*-dichlorobenzene, b. p. 177—181° (corr.), is used. The furnace end of the boiler is provided with an asbestos ring which fits closely round the combustion tube, and the portion of the combustion tube in the boiler is loosely packed with asbestos. (For the construction of these boilers the author is indebted to Mr. J. L. Osborne.)

Owing to the much larger contact surface presented by the macro- as compared with the micro-filling, the Mariotte flask adopted by Pregl is discarded. Soda-lime and calcium chloride are used both in the purifying train and in the absorption tubes. The combustion is carried out in the ordinary way, care being taken not to heat too strongly that portion of the furnace immediately before the copper boiler. The silver filling and lead peroxide asbestos suffice for about 10 combustions.

The method has been thoroughly tested for many types of substances, including those containing halogens and sulphur, and both amino- and nitro-groups; representative analyses for such substances are: Chlorobenzene-2 : 4 : 6-trisulphonyl chloride (Found: C, 17·7, 17·7, 17·5; H, 0·9, 0·7, 0·6. Calc.: C, 17·6; H, 0·5%). Acetanilide (Found: C, 70·9, 71·1; H, 6·6, 6·5. Calc.: C, 71·1; H, 6·7%). *p*-Chloronitrobenzene (Found: C, 45·6, 45·5, 45·5, 45·8; H, 2·5, 2·5, 2·4, 2·6. Calc.: C, 45·7; H, 2·5%). 2 : 4-Dinitrotoluene (Found: C, 46·2, 46·0, 45·9; H, 3·2, 3·4, 3·4. Calc.: C, 46·1; H, 3·3%). Picryl chloride (Found: C, 29·1, 28·9, 29·1; H, 1·2, 0·9, 0·9. Calc.: C, 29·15; H, 0·8%).—MELBOURNE UNIVERSITY. [*Received, September* 19*th*, 1927.]

The Electroendosmosis of Aqueous Solutions through Glass Diaphragms. By HORACE CHARLES HEPBURN.

FAIRBROTHER and VARLEY (this vol., p. 1584) have measured the electroendosmosis of dilute hydrochloric acid through a diaphragm of sintered Jena " Geräte " glass powder, and their results lead them to conclude with Lachs and Kronman (*Rocz. Chem.*, 1926, **6**, 641) that the interfacial equilibrium between glass and aqueous solutions is not a true one, but changes with time. They give the results of two series of electroendosmotic determinations with dilute hydrochloric acid, the second series consisting of a repetition of the first series after the diaphragm had been " carefully cleaned." In each series, the results were " quite concordant among themselves," but the electrokinetic potential was throughout less negative in Series II than in Series I. No reference is made to the lowering of electrokinetic potential produced by given concentrations of hydrochloric acid; when this factor is considered, however, the two series of results show a remarkable similarity. The lowering is given by $\zeta_0-\zeta_c$, where ζ_0 and ζ_c represent the electrokinetic potential at concentrations zero and c, respectively; and values for $\zeta_0-\zeta_c$, obtained from Fairbrother and Varley's results, are given in the subjoined table. It will be observed that, except in the case of the most dilute solution (where the potential lowering is small and the value is affected to a greater extent by experimental error), the two series of values are in satisfactory agreement.

	Lowering of electrokinetic potential (volt).	
Solution.	Series I.	Series II.
$N/5000$-HCl	0·0041	0·0075
$N/1250$-HCl	0·0113	0·0111
$N/400$-HCl	0·0163	0·0169
$N/100$-HCl	0·0310	0·0309

Thus, contrary to the view of Fairbrother and Varley, there appears to be little indication from these results of any change in the effective size of the diaphragm pores corresponding to a progressive swelling process at the glass surface; on the other hand, it seems probable that these authors, in the process of cleaning their diaphragm, failed to remove the last traces of adsorbed electrolyte. The difficulty in bringing a diaphragm back to its original state after treatment with an electrolyte solution has been referred to by Freundlich and von Elissafoff (*Z. physikal. Chem.*, 1912, **79**, 385), who found, in some instances, that repeated treatment with concentrated nitric acid was necessary; similar treatment of a diaphragm of powdered glass, however, introduces the difficulty of removing the final traces of acid by washing with water. Fairbrother and Varley were able to reproduce the value of ζ obtained in the initial determination with water by treating the diaphragm with nitric acid, but subsequent determinations with dilute hydrochloric acid gave results deviating from the original values.

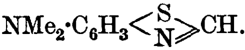
The author (*Proc. Physical Soc.*, 1926, **38**, 363; 1927, **39**, 99) has surmounted the difficulty in bringing a diaphragm back to its original state after treatment with an electrolyte solution by employing an entirely fresh diaphragm for each series of observations. When this procedure was followed, it was possible to obtain concordant results in determinations made at intervals over a period of several months.—BIRKBECK COLLEGE (UNIVERSITY OF LONDON).

[*Received, September 2nd*, 1927.]

The Use of Hydrogen Peroxide for Iodine and Other Substitutions in Aromatic Compounds. By JAMES ERNEST MARSH.

HYDROGEN peroxide may be used to facilitate substitutions. For example, a solution of phenol in alcohol with the calculated quantity of iodine is warmed and hydrogen peroxide (30%) is added, the colour of the iodine gradually disappears, and 2 : 4 : 6-tri-iodophenol crystallises. Similarly β-naphthol yields 1-iodo-β-naphthol in quantitative amount.

It is not necessary to start with iodine in the free state. When phenol is dissolved in glacial acetic acid, the requisite amount of potassium iodide added, and the solution heated, the addition of hydrogen peroxide brings about the quantitative separation of tri-iodophenol; replacement of the potassium iodide by a metallic bromide gives tribromophenol, and replacement by hydrochloric acid gives trichlorophenol.

The thiocarbimido-group can be introduced as follows : Dimethylaniline and potassium thiocyanate in molecular proportion are dissolved in glacial acetic acid and hydrogen peroxide is added gradually. The solution becomes hot and, on cooling, the compound $C_9H_{10}N_2S$ crystallises. It may be recrystallised from alcohol and forms colourless plates, m. p. 73° (Found : C, 61·0; H, 5·7; N, 15·7; S, 18·3. Calc. : C, 60·6; H, 5·6; N, 15·7; S, 18·0%). This compound was obtained by Söderbäck (*Annalen*, 1919, **419**, 275) by the action of an ethereal solution of thiocyanogen on dimethylaniline. It is probable that it is not a simple thiocyanogen derivative of dimethylaniline, but that it is identical with the compound which Schmidt synthesised (*Ber.*, 1906, **39**, 2409) by the action of nitrous acid on the condensation product of formaldehyde with *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid, and to which he assigned the constitution  $NMe_2{\cdot}C_6H_3{<}\overset{S}{\underset{N}{}}{>}CH$.—UNIVERSITY MUSEUM, OXFORD.

[*Received, October 28th*, 1927.]