

8772 P

Micro-Determination of Fluorine.

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The author's¹ modification of the Willard-Winter² method has been adapted to the determination of small quantities of fluorine. The distillation of H_2SiF_6 is carried out in the usual manner except that a 50 cc. distilling flask, 0.1 gm. quartz and 5 cc. 60% perchloric acid are employed. The temperature of the flask contents is maintained at 140° , and 150 cc. of distillate are collected. The water employed is freshly boiled after redistillation from alkali. The distillate is made alkaline to phenolphthalein, evaporated to a small volume, rendered just acid to the indicator, and diluted to 10 cc. One cc. aliquots are transferred to 5 cc. vials (such as those in which dentists receive gold foil). The addition of an equal volume of alcohol is omitted in order to permit a direct relationship between the fluorine content of the aliquots and the volume of $\text{Th}(\text{NO}_3)_4$ solution used for their titration and to render inoperative the effect of HClO_4 on the determination of more than 5 γ (micrograms) F. If the sample contains less than 5 γ F, 6 gm. NaClO_4 are added to the charge in the distilling flask, the distillate evaporated to about 5 cc. and the aliquots taken by weight. NaClO_4 reduced the amount of HClO_4 volatilized during the distillation of H_2SiF_6 . One drop of 0.05% sodium alizarin sulphonate is added to the aliquots and, after split drops of appx. 0.03 *N* HCl are added until the indicator has a light orange color, one drop of buffer soln. (1 molar monochloroacetic acid and 1 molar sodium monochloroacetate) is introduced. The fluorine is titrated with appx. 0.0004 *N* $\text{Th}(\text{NO}_3)_4$ (1 cc. = 7.8 γ F) to the appearance of a barely perceptible pink color which matches that of a titrated standard solution containing 5 γ F. The $\text{Th}(\text{NO}_3)_4$ solution is standardized daily by titration of 1 cc. volumes of solutions containing 10, 5 and 1 γ F. The results are substituted in the two-point equation for a straight line and the titration blank calculated.

Five analyses each of 25 and 10 γ quantities of F gave an average recovery which was 1.4% low. Seven distillation blank determinations in which 25 and 10 γ of fluorine were added to the receiver

¹ Armstrong, W. D., *J. Am. Chem. Soc.*, 1933, **55**, 1741.

² Willard, H. H., and Winter, O. B., *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7.

contents gave an average recovery 2.5% low. The quantity of fluorine in each aliquot titrated was one-tenth the total in distillate. Four analyses each of 5 and 2 γ quantities gave results 1.5% low while corresponding distillation blank determinations averaged 0.5% low.

Four analyses of a quantity of mixed sound human enamel gave the results 0.0163, 0.0154, 0.0164, 0.0160% F. Three determinations were made in which 10 micrograms F were distilled from the residue in sample. The average recovery was 10.1 γ F. Three analyses in which the distillate was redistilled and one in which it was twice redistilled showed 0.0158% F in the enamel. These latter results indicate that phosphate or any other substance in enamel is not volatilized in a sufficient quantity to affect the results.

The average recovery of 5 γ F added to enamel was 4.8 γ . Two determinations using NaClO_4 showed the enamel to contain 0.0160% F. A sample of C.P. " $\text{Ca}_3(\text{PO}_4)_2$ " contained 0.622% F and one of C.P. $\text{Ca}(\text{H}_2\text{PO}_4)_2$ contained 0.013% F. The method has been successfully applied to the determination of F in dentin and will be extended to other biological material.

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Comparative Studies of Gonadotropic Hormones.* 5. Growth Response of Rat Mammary Glands in Chronic Experiments.

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A description of the changes induced in the ovaries and hypophysis of female rats following the prolonged administration of gonadotropic extracts prepared from sheep anterior pituitary glands and blood of pregnant women was given in the fourth report of this series (Fluhmann¹). The present communication deals with the gross and microscopic effects observed in the mammary glands of these rats.

Sheep Anterior Pituitary Extracts. Six rats received daily injections for 63 days. Breast biopsies showed proliferation of ducts

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¹ Fluhmann, C. F., *Proc. Soc. Exp. Biol. and Med.*, 1936, **34**, 691.