

## Determination of Fluorine in Wool treated with Fluorides

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FLUORIDES are toxic to Clothes-moth and carpet beetle larvae, and impregnation of keratinous materials, *e.g.*, wool, hair and feathers, with solns. of organic and inorganic fluorides is a well-known method of rendering these materials indigestible to, and hence immune from attack by, pests of this type; the method is covered by numerous patents.<sup>1</sup> Also fluorides, particularly sodium and ammonium silicofluoride, are the active constituents of a number of proprietary moth-proofing agents at present on the market. The treatment is most successful when the materials are not required to undergo further wet-processing or household washing during the period of protection, *e.g.*, hosiery liable to prolonged storage after manufacture, stuffing materials, furnishings and dress suitings.

The method usually adopted for testing the efficiency of moth-proofing agents consists in bringing the treated material into contact with a number of vigorous young moth-larvae (Clothes-moths or Casemakers, the former being preferable), which have no other source of food, storing under suitable conditions and examining at intervals; a useful technique is that described by Stiteler.<sup>2</sup> The moth-proofing is assessed by (1) the damage suffered by the sample, (2) the effect on the larvae, and (3) the quantity of excrement present. This method, which gives clear-cut results for adequately proofed and unproofed materials and reasonably reproducible results for intermediate degrees of proofing, is unfortunately lengthy, 14–30 days being necessary for a satisfactory test. By examining the resistance to moth-larvae of samples of wool containing different amounts of fluorine, we in collaboration with R. S. Hartley (in the press) have shown that materials containing *ca.* 0.2% of fluorine are satisfactorily immune from attack. Thus the fluorine content of the material is a useful indication of the degree of moth-proofing, and by using the method described below for the determination of fluorine in wool it has been found possible to assess the moth-resistant properties of yarns and fabrics treated with inorganic fluorides in a comparatively short time and to eliminate much testing with moth-larvae.

**REVIEW OF METHODS.**—For the determination of micro-quantities of fluorine in biological material it is necessary to ash the sample and then to recover the fluorine, usually as fluosilicic acid, by distillation with a non-volatile acid. In the method originally described by Willard and Winter,<sup>3</sup> the ashed material is distilled with perchloric acid at 135° C., and the fluorine in the distillate is estimated by titration with thorium nitrate in 50% ethanol, zirconium alizarin sulphionate being used as indicator. This method, with numerous modifications, has since been widely used for the determination of fluorine in foods, rocks and water. A study of the literature, which is too extensive to be reviewed here in detail, indicates that the principal factors which have caused difficulty in the use of the method are: (1) loss of fluorine by volatilisation during ashing, (2) interference with the fluorine estimation by the distilling acid (which cannot be completely prevented from passing into the distillate) and (3) the determination of the optimum conditions for the estimation of fluorine in the distillate.

(1) *Ashing.*—A considerable loss of fluorine was reported by Hoskins and Ferris<sup>4</sup> when ashing the sample at 800° C. for even a short time. Rempel,<sup>5</sup> ashing sodium fluoride in presence of sodium carbonate, observed a considerable loss at 500° C., and at 800° C. only a trace of fluorine remained. Calcium oxide and magnesium oxide and acetate have been used by several workers<sup>6,7,8,9</sup> as fixatives for fluorine during ashing, and Rempel,<sup>5</sup> ashing in presence of calcium oxide or wine ash (which contained calcium and magnesium oxides), showed that no loss of fluorine occurred up to 600° C. We have ashed the samples below red heat in presence of excess sodium carbonate (to neutralise any residual acid in the wool) without any addition of calcium or magnesium, and have extracted the ash with water to separate any traces of carbon remaining and other insoluble matter; the recoveries of fluorine added to wool as sodium and chromium fluorides were satisfactory. As an additional check on the ashing method, 2 mg of fluorine as sodium fluoride were heated in presence of sodium carbonate at the temp. used for ashing the wool samples; 1.94 and 2.00 mg were recovered in duplicate expts., showing that, in absence of wool, no substantial loss of fluorine occurred under the ashing conditions employed. Calcium,

derived from waters or from lime used in pulling wool from hides, is normally present as sulphate, carbonate or calcium soap in all processed wool. The calcium in the cloth used in the recovery expts. was 0.06% (on the weight of wool), and did not interfere with the recovery of the fluorine by the technique described.

(2) *Distillation*.—For the distillation of fluorine as fluosilicic acid, sulphuric and perchloric acids have been used, and the temperature in the distilling flask has varied from 125° to 150° C., leading to a wide variation in the amount of sulphuric or perchloric acid in the distillate. The majority of workers have used perchloric acid, probably because it has a less adverse effect in the fluorine titration than an equiv. amount of sulphuric acid.<sup>4,8,10</sup> Van der Merwe,<sup>11</sup> by maintaining the distillation temp. at 130° C., was able to restrict the total acidity of 200 ml of distillate to 3 ml of *N*/100 acid. We have found 130° C. to be too low for complete recovery of fluorine, but at 135–140° C. adequate recovery of fluorine in amounts up to 1.5 mg was obtained in 200 ml distillate, the total acidity of which did not exceed 15 ml of *N*/100 acid. This amount of acid is of the same order as that reported by Dahle, Bonnar and Wichmann,<sup>13</sup> and does not interfere with the subsequent determination of fluorine.

(3) *Determination of fluorine in the distillate*.—The original technique of Willard and Winter<sup>3</sup> has been modified by many workers, the chief features that have been examined being the nature and concn. of the indicator, the nature of the medium, *i.e.*, whether aqueous or 50% ethanol, and its *pH*, and finally the influence of salts, *e.g.*, chlorides, sulphates and perchlorates. The method used by us is substantially the same as the back-titration method originally suggested by Dahle *et al.*,<sup>12,13</sup> and later used by Van der Merwe,<sup>11</sup> which depends upon the bleaching of thorium-alizarin lake through preferential formation of thorium fluoride. In this method the total acidity of the aqueous test soln. is adjusted to 2 ml of *N*/20 acid per 50 ml (*pH* 2.7), the perchloric acid present in the distillate (determined on a separate aliquot portion) being used to contribute to this acidity, thus preventing neutralisation of the distillate and avoiding the effect of sodium perchlorate.

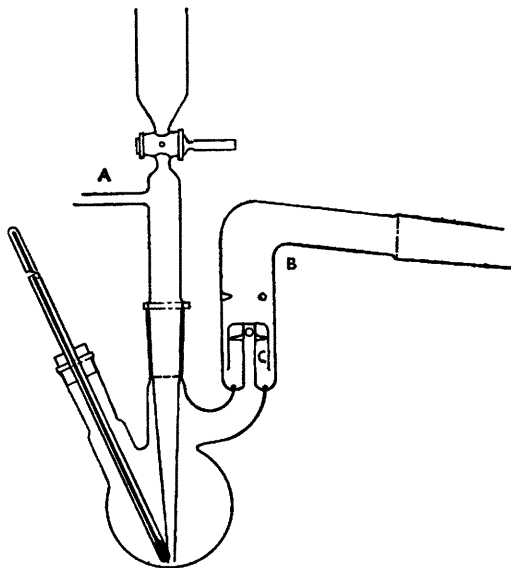


Fig. 1

**PROCEDURE**.—Completely moisten 0.5–5 g of wool (containing 0.25–5.0 mg of fluorine) with 10 ml of *N*/2 sodium carbonate in a platinum dish or crucible. Dry and ash in a muffle below red heat. Ashing is assisted if, after charring, the residue is moistened with water and dried and the ashing is continued; it is complete in *ca.* 1 hr. Extract the residue with water, filter and make up to 50 ml.

The distillation unit comprises a 50-ml distilling flask (see Fig. 1) of a modified Claisen pattern. The side-tube (A) permits the introduction of steam from a boiler. The side-neck (B), which contains an anti-splash device (C), is connected to a Liebig condenser, the distillate being collected in a 250-ml conical flask by means of an adaptor which dips below the level of the liquid in the flask. The distilling flask rests in a hole (diam. 1½ in.) in a 6-in. square of cement-asbestos board, and is heated by means of a micro-burner; this prevents direct heating of the flask above the level of the liquid.

Introduce a suitable aliquot portion (5 or 10 ml containing 0.10–1.50 mg of fluorine) of the aqueous extract from the ash into the distilling flask and add 0.01 g of silica and 3 glass beads (diam. 0.2 in.); if a larger portion is used, preliminary boiling down is necessary. Add 10 ml of 60% perchloric acid through the tap funnel and steam-distil, maintaining the temp. at 135–140° C. by regulation of the micro-burner and the steam flow. Collect 200 ml of distillate (about 1¼ hr.) and make up to 250 ml.

Titrate 10 ml of the distillate with *N*/100 sodium hydroxide, using 0.01% sodium alizarin sulphonate in a sat. soln. of 1,2,5,8-tetrahydroxyanthraquinone<sup>3,11</sup> as indicator.

To a second portion of distillate (containing preferably 10–20  $\mu\text{g}$  of fluorine) in a Nessler tube add sufficient  $N/20$  hydrochloric acid to make the total acidity equal to 2 ml of  $N/20$  acid. Add 1 ml of indicator (as above) followed by  $N/500$  thorium nitrate (exact strength not important) from a burette until a clear pink colour, free from yellow tone and suitable for colorimetric matching is developed (0.5–3 ml of thorium nitrate), and make up to 50 ml. Put into a second Nessler tube 2 ml of  $N/20$  hydrochloric acid, 1 ml of indicator and approx. 20 ml of water, and then the same vol. of  $N/500$  thorium nitrate as was used for the test. Add standard sodium fluoride\* (1  $\mu\text{g}$  of fluorine per ml) until a colour match is obtained, final comparison being made in the same vol. Finally, make up similarly 2 more tubes, but add initially the vol. of standard sodium fluoride used in the back-titration so that final comparison with the standard is made under identical conditions. If necessary, add 0.5 ml sodium fluoride to the darker tube if matching is still imperfect. Comparison is best effected in north light by standing the tubes on a white tile and surrounding them by white card to form a box 6 in. square and at least as high as the Nessler tubes. The estimation is sensitive to 0.5 ml of standard sodium fluoride and its accuracy is thus 2.5% for 20  $\mu\text{g}$  of fluorine and 10% for 5  $\mu\text{g}$  of fluorine.

**RESULTS AND DISCUSSION.**—The influence of distillation temp. on the acidity of the distillate and the recovery of fluorine, added directly to the distillation flask as sodium fluoride, was determined in a series of expts. in which 1 mg of fluorine was added in each of a series of distillations at temp. ranging from 125° to 145°. The results showed that at 135°–140° C., resulting in an acidity equiv. to 0.5 ml of  $N/100$  per 10 ml of distillate, the recovery was from 97.5 to 100%; this temp. was therefore used in all succeeding distillations. In further expts. in which 0.1–1.5 mg of fluorine was added to the contents of the distillation flask, the recoveries ranged from 95.0 to 100%.

Next, known quantities of fluorine were added as sodium or chromium fluoride soln. to 1 g of scoured white woollen cloth in a platinum dish, the whole was evaporated to dryness, and the fluorine was determined by the above method; the results are given in Table I.

TABLE I  
RECOVERY OF FLUORINE ADDED TO WOOL

Fluorine added, mg	Acidity, ml of $N/100$ per 10 ml	Fluorine recovered mg	Recovery %
Fluorine added as sodium fluoride			
0.5	0.56	0.44	88.0
0.5	0.42	0.44	88.0
1.0	0.50	0.94	94.0
1.0	0.42	1.00	100.0
2.0	0.50	1.88	94.0
2.0	0.30	1.88	94.0
5.0	0.48	4.88	97.6
5.0	0.52	5.00	100.0
Fluorine added as chromium fluoride			
0.975*	0.52	0.94	96.5
0.975*	0.50	0.94	96.5
1.95*	0.54	1.94	99.5
1.95*	0.46	1.94	99.5

\* Standardised against sodium fluoride by distilling chromium fluoride soln., assuming 100% recovery in distillation.

The amount of fluorine present in moth-proofed wool would not normally exceed 0.5% (on the weight of wool) and the results show that these small amounts can be satisfactorily determined on a small sample of wool with an accuracy of *ca.* 5%, which is adequate for control of the fluoride moth-proofing process. For wool with a fluorine content less than 0.1%, it is recommended that a larger sample be used.

Finally, determinations were made of 2 mg of fluorine added to wool materials that had undergone normal processing, thus containing residual substances which might

\* The sodium fluoride used throughout as the standard in the colorimetric estimation was a 10- or 100-fold dilution of that used for the various recovery determinations; hence the results are not influenced by the purity of the sodium fluoride, which contained 44.7% of fluorine determined by the lead chlorofluoride method<sup>14</sup> (sodium fluoride requires 45.2%).

interfere with the recovery of fluorine; the results, with particulars of the samples used, are as follows:

Black worsted, chrome dyed (Cr, 0.43%).	Fluorine recovered, %	94.0; 100.0
Khaki woollen, chrome dyed (Cr, 0.30%).	" "	100.0; 100.0
(Ca, 0.06%).		
Knitting yarn, acid dyed (sulphuric acid, 2.64%).	" "	97.5; 97.5

**SUMMARY.**—A method for the determination of fluorine in wool moth-proofed by treatment with fluorides is described. The sample is ashed, and the fluorine is distilled from the ash as fluosilicic acid and estimated colorimetrically by its decolorising action on thorium-alizarin lake. Satisfactory recoveries of known amounts of fluorine added to wool have been obtained. The method is designed to determine up to 0.5% of fluorine (on the weight of wool) with an accuracy of the order of 5%.

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### DISCUSSION

Mr. R. MILTON said that his laboratory had been working for some months on the determination of fluorine, and had encountered several difficulties. First, distillation should be prolonged so as to make certain that all fluorine came over, particularly if any pptd. silica was present, as it almost always was after fusion. Secondly, there was always a fluoride blank of about 5 $\mu$ g; this was not due to rubber bungs as suggested by some American writers, since it occurred with all-glass apparatus. They had also investigated dyestuffs as alternatives to alizarin, and had found Solochrome Brilliant Blue BS much superior. The lake formed with thorium was blue, giving a more definite colour change from yellow to blue on titration. The reaction with thorium, dye and fluorine was immediate, whereas the alizarin reaction was delayed. Moreover, the titration value was increased, so that about three times as much standard thorium soln. was used with a given amount of fluorine.

Mr. D. D. MOIR said that in recent months he had determined the amount of fluorine in large numbers of baking powders, egg substitute powders and similar types of food. A difficulty occurred if chloride was present in the article, since hydrochloric acid distilled over and increased considerably the acidity of the distillate. It had been suggested that silver sulphate should be added to the distilling flask, to retain the chloride as silver chloride and he had found this to be reasonably satisfactory. He asked whether the authors had had any experience with this or other methods for overcoming this difficulty. The method of determining fluorine that he had used was similar to that of the authors, which closely followed that of recent American workers.

Mr. F. L. OKELL suggested that, as fluorides were sometimes present in resistance glass, the "blank" might possibly be derived from the apparatus.

Mr. F. F. ELSWORTH, replying to the President, said that they had had no experience of the zirconium-alizarine method. The most recently published methods for determining fluorine used thorium nitrate almost exclusively and the optimum conditions had been the subject of a thorough study which had not been applied to the zirconium method. The fluorine blank on a 10- or 20-ml. aliquot portion of the distillate did not exceed 0.5 $\mu$ g. Almost complete recovery of fluorine had been obtained by collecting 200 ml of distillate, no appreciable amount of fluorine being found in a second portion of 200 ml of distillate. In the back-titration method, the end-point was not determined by a colour change from yellow to pink, but by matching solutions of pink colour. Loss of fluorine had been observed at temps. as low as 500° C.; they had tended towards incomplete ashing rather than risk any loss of fluorine. The white precipitate sometimes observed during titration was undoubtedly thorium fluoride, but with the amount of fluorine (10–12 $\mu$ g) present in the final determination in their method no turbidity had been observed. Chloride was not normally present in wool in amounts likely to cause any interference in the estimation, and hence no precautions had been taken to retain hydrochloric acid in the distilling flask.