A SPRAYING REAGENT FOR ANIONS

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During a search for a suitable reagent for the detection of some sulphur–nitrogen compounds *e.g.* sulphamide on filter paper, it has been found that a mixture of sodium fluoresceinate and silver nitrate in aqueous solution will produce colour reactions with many of the common anions. This has been reported as a test for Cl(I), Br(I) and I(I) previously, but the anions were observed as dark spots on a fluorescent background[1]. Lower concentrations of silver nitrate and fluorescein will produce this effect.

The silver fluoresceinate produced on mixing aqueous solutions of silver nitrate and sodium fluoresceinate is red in colour and it does not fluoresce under ultraviolet light. In general, when the NH_4^+, Na^+, or K^+ anion salt of the acid is sprayed with the reagent, a yellow spot on a red background is produced if the anion forms an insoluble silver salt:

$$\text{Ag. fluor.} + MA \longrightarrow \underset{\text{yellow}}{\text{M. fluor.}} + AgA \downarrow$$

if M = NH_4^+, Na^+, K^+, H^+.

Often this spot will fluoresce under ultraviolet light. The action of light will also often produce secondary reactions, such as the reduction of the silver anion salt to silver, which may give further colour changes. Thus chloride ion yields a yellow fluorescent spot which, by the action of light, turns green owing to the blue colouration produced by the breakdown of silver chloride to metallic silver.

It has been found that some anions which yield soluble silver salts will nevertheless give a colour reaction with the reagent, although it is not usually as distinct or as sensitive as for the insoluble silver salts.

The *spraying reagent* was composed of one part of 10 % w/v aqueous silver nitrate solution and five parts of 0.2 % w/v sodium fluoresceinate in absolute alcohol. 1 % w/v solutions of various anions were spotted on Whatman No. 1 filter paper, dried and then sprayed. The results are tabulated in Table I.

Also CNS(I), F(I), Cl(I), Br(I), I(I), $SO_2(NH_2)_2$, SO_4(II), $NH[SO_3(I)]_2$, and NH_2SO_3(I) were detected as very distinct spots on chromatograms which were eluted using the standard chromatographic solvents, and 1 % w/v anion solutions[2].

The colour produced by the spray seems to depend upon the anion concentration present in the spot and also upon the concentration of silver fluoresceinate in the spray. With higher anion concentrations it is likely that a yellow spot will be produced with all species. Thus a higher concentration of fluoride will yield a yellow spot

TABLE I

Anion	*Cation*	*Coloration in visible light*	*Coloration under ultraviolet light*
Fluoride	Sodium	Dark red-brown spot after U.V. light	Faint yellow fluorescence
Chloride	Potassium	Green in visible	Yellow fluorescence
Bromide	Potassium	Green in visible	Yellow fluorescence
Iodide	Potassium	Yellow	Yellow-green fluorescence
Bromate	Potassium	—	Yellow fluorescence
Iodate	Potassium	—	Faint yellow fluorescence
Periodate	Potassium	No reaction	No reaction
Sulphite	Sodium	Yellow	Yellow fluorescence
Sulphate	Ammonium	Light brown	Green colour
Thiosulphate	Sodium	Green	Dark blue
Dithionate	Sodium	Action of U.V. light forms dark red spot when viewed under visible light	
Trithionate	Potassium	Green	Dark blue
Metabisulphite	Sodium	White	Light green
Nitrite	Sodium	Yellow	Yellow fluorescence
Borate	Sodium	Action of U.V. light causes spot to change from yellow to red	Yellow fluorescence
Carbonate	Sodium	Green changing to red with time	Green-yellow fluorescence
Thiocyanate	Ammonium	Yellow	Yellow fluorescence
Ferrocyanide	Potassium	Yellow	Yellow fluorescence
Ferricyanide	Potassium	—	Dark spot
Formate	Potassium	Dark brown	Dark spot
Acetate	Sodium	Slowly developing red spot	—
Oxalate	Ammonium	Light brown	Yellow fluorescence
Tartrate	Potassium	Yellow	Yellow fluorescence
Citrate	Sodium	Yellow	Yellow fluorescence
Phthalate	Potassium hydrogen	White	Dark spot
Molybdate	Ammonium	Pale yellow	Light green fluorescence
Vanadate	Ammonium	Yellow	Green
Hydroxide	Sodium	Green	Yellow-green fluorescence
Bicarbonate	Potassium	—	Green fluorescence
Lactate	Ammonium	Light brown	Light green
Arsenate	Sodium	Light brown	Dark green
Arsenite	Sodium	Light brown	Dark green
Phosphate	Sodium dihydrogen	Blue-green	Blue
Phosphate	Disodium hydrogen	Green	Yellow-green fluorescence
Pyrophosphate	Sodium	Yellow	Yellow fluorescence
Triphosphate	Sodium	Brown-red	—
Trimetaphosphate	Sodium	Brown-red	—
Tetrametaphosphate	Sodium	Brown-red	—
Monothiophosphate	Sodium	Green	Dark spot
Dithiophosphate	Sodium	Green	Dark spot
Trithiophosphate	Sodium	Yellow	Dark spot
Imidodisulphonate	Ammonium	Yellow	Yellow fluorescence
Sulphamate	Ammonium	Yellow	Yellow fluorescence
Sulphamide	—	Yellow	Yellow fluorescence

which is fluorescent under ultraviolet light. Too low a concentration of fluorescein results in white non-fluorescent spots, and hence there is a loss of sensitivity whereas too little silver nitrate will give indistinct spots which may be blurred.

It is essential that the chromatogram be dried thoroughly before spraying so that all interfering substances such as ammonia or hydrochloric acid are removed. For this reason the spray cannot be used on chromatograms which have been eluted with a solvent containing a comparatively involatile substance, such as trichloroacetic acid, which will give a yellow fluorescence with silver fluoresceinate under ultraviolet light.

There is no reason why other metal fluoresceinates should not be used as spraying reagents if their colour differs from that of the free fluorescein or, alternatively, if the metal fluoresceinate is non-fluorescent. Thus lead fluoresceinate may be used as a reagent to detect the halides. These all give yellow fluorescent spots (except iodide, which yields a canary-yellow, non-fluorescent spot) on an orange background.

It can be seen that the spraying reagent described can be used to detect many of the common anions—in particular those which will form insoluble silver salts.

SUMMARY

A mixture of sodium fluoresceinate and silver nitrate in aqueous solution is described as a spraying reagent which can be used to detect many of the common anions—in particular those which form insoluble silver salts.

REFERENCES

1 F. H. BURSTALL, C. R. DAVIES, R. P. LINSTEAD AND R. A. WELLS, *J. Chem. Soc.*, (1950) 516.
2 E. BLASIUS, *Chromatographische Methoden in der analytischen und präparativen anorganischen Chemie*, F. Enke Verlag, Stuttgart, 1958, p. 284.