

SHORT COMMUNICATIONS**A note on the detection of sulphate ions on paper chromatograms**

The detection of substances on paper chromatograms requires a reaction which distinguishes the substance from the paper background. Usually colour reactions are employed, and when these do not exist a coloured spray which distinguishes background from substance is employed.

For sulphate ions no satisfactory reaction has so far been found, although one could be envisaged using a  $\text{Ba}^{++}$  spray followed by a colour reaction for the excess  $\text{Ba}^{++}$  on the background. The  $R_F$  values obtained by several authors in acid media were measured with radioactive  $\text{H}_2^{35}\text{SO}_4$ .

In this note we wish to describe a simple reaction for sulphates when these are developed in solvents containing HCl.

It was noticed that when the chromatogram was dried in an air oven black spots were formed wherever  $\text{H}_2\text{SO}_4$  was left after the solvent had evaporated. This reaction is reliable if carried out as described in the experimental part and if the paper is viewed under ultraviolet light, it is sensitive to 5  $\gamma$  of  $\text{H}_2\text{SO}_4$  per spot.

*Experimental*

5  $\mu\text{l}$  of the solution to be analysed are placed on Whatman No. 1 paper and developed by the ascending method with butanol-1 N HCl for 8 hours. The paper is then removed from the developing chamber and immediately placed in an air oven and dried at 105° C.

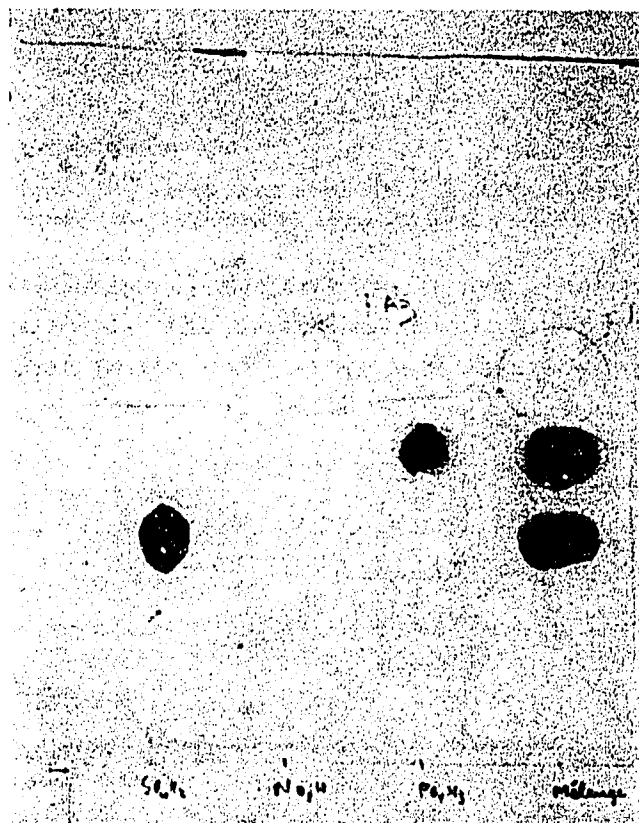


Fig. 1. A chromatogram developed with butanol-1 N HCl and heated for 10 min at 105°. [From left to right: sulphuric acid, nitric acid, phosphoric acid, and a mixture of all three.

After the solvent has evaporated (approx. 10 min) sulphates form black spots. Fig. 1 shows a chromatogram thus treated. The spots from left to right are  $N/10$   $H_2SO_4$ ,  $N/10$   $HNO_3$ ,  $N/10$   $H_3PO_4$  and a mixture of all three.

Phosphoric acid also produces a darkening and nitric acid a fluorescent spot in ultraviolet light. Both can, however, be distinguished by their  $R_F$  values from sulphate.

This reaction, simple as it seems, is, however, possible only under controlled conditions, and we shall enumerate the factors that may interfere.

The chromatogram may not be developed for more than 8 hours. Chromatograms that were left overnight, gave only a uniform darkening of the whole sheet. Likewise, chromatograms that were allowed to dry overnight also showed uniform darkening. In both cases the prolonged contact with HCl seems to produce considerable decomposition of the paper.

On the other hand the reaction works well, irrespective of whether an alkali sulphate, an alkaline earth sulphate, or free sulphuric acid, is chromatographed. In the case of the salts the cation stays in the region of the  $R_F$  0-0.1 and thus cannot interfere with a reaction that seems to be that of free  $H_2SO_4$ .

The sensitivity was tested by making successive dilutions of sulphuric acid and running them on the same sheet. A dark spot is formed with as little as 20  $\gamma$  but when the paper is held under ultraviolet light even 5  $\gamma$  may still be detected as a fluorescent spot.

The fluorescence has been observed to fade with time, while the dark colour appears to be quite stable.

We believe that this reaction may be reliable in testing for sulphates.

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### **Bemerkung zur Mikro-Jodbestimmung nach Bowden, Maclagan und Wilkinson**

Nach dem von BOWDEN *et al.*<sup>1</sup> angegebenen Verfahren (Reaktion mit Cer(IV)Sulfat und arseniger Säure) lassen sich z.B. 0.01 Mikrogramm KJ und 0.1 Mikrogramm Thyroxin auf dem Papierchromatogramm erkennen und zwar als weisse Flecken auf hellgelbem Grund. Allerdings lassen sich Flecken, die von den angegebenen Substanzmengen herrühren, wegen des geringen Kontrastes nur schlecht photographieren.

Dem kann abgeholfen werden, indem man das Chromatogramm in Phenoldämpfe bringt, wodurch der gelbe Hintergrund hell- bis dunkelbraun wird, was die Flecken ausgezeichnet hervor- treten lässt.

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