Paper Chromatography of Some Sulfinic Acids and Sulfonylchlorides

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Feigl\(^1\) used the orange-red insoluble iron(III) salt of benzenesulfonic acid as spot test. Gilman and Abbot\(^2\) characterized p-toluenesulfonic acid by the melting point of thallium dichloride-p-toluenesulfinate.

It has now been found that alkyl and arylsulfinic acids (or their salts) react with zinc chloride stabilized tetrazo-o-dianisidine

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\begin{array}{c}
\text{Feigl}\quad \text{(Echtblau B Salz, E. Merck)}
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OCH\(_3\) OCH\(_2\)

\[\text{N}_2\quad \text{ZnCl}_4^{2-}\]

[To be continued...]

Sulfinic acids:
Benzenesulfinic acid and salts (Hoechst)
p-Toluenesulfinic acid (Bofors, Sweden)
2,6-Dichloro-p-toluenesulfinic acid (prepared according to Ref.\(^2\))
Ethansulfinic acid, sodium salt (Hoechst)
2-Naphthalenesulfinic acid

Sulfonylchlorides:
p-Toluenesulfonylchloride (Bofors, Sweden)
2,6-Dichloro-p-toluenesulfonylchloride (Bofors)
2-Napthalenesulfonylchloride (Merck, Germany)
Methansulfonylchloride (Fluka, Switzerland)

Whatman No. 1 filter paper for chromatography, 24 x 40 cm in size was used. The chromatograms were developed in a suitably sized glass tank equipped with stainless steel racks from which the paper was suspended so as to dip into the solvent, which was placed at the bottom of the tank. The chromatograms were developed for 16 h at 20°C. The solvent consisted of chromatographically pure n-butanol, n-propanol and water (1:1:1).

Concentration standards, 5 x 10\(^{-4}\) and 5 x 10\(^{-3}\) M, were prepared from sulfinic acid salts in distilled water.

The sulfonylchlorides were dissolved in dioxan, ethanol or benzene. Liquid sulfonylchlorides were used directly, without dilution.

Detection of sulfinic acids. The standard solutions were applied from a glass capillary on a starting line 3 cm from the bottom edge of the paper sheet and 2 cm intervals between spots, by touching the end of the capillary to the paper and withdrawing it when the spot had attained the required size. The spots could be made visible after developing and drying the chromatogram, by spraying it with a dilute solution of potassium permanganate, when the sulfinic acid appeared as a white spot on the purple background. After some time, however, the purple background faded out. A spray

Fig. 1. Quantitative estimation of the amount of p-toluenesulfinic acid as a function of spot area.
consisting of a solution of dinitrophenylindole gave white spots on a blue background. Neither of these reagents are specific for the sulfinic group. The insoluble yellow dye formed by spraying with a 0.25—0.5% solution of the stabilized tetrazotized o-dianisidine, seems to be very specific. Darkening of the white background on storage can be prevented by washing the chromatogram with cold distilled water.

Detection of sulfonylchlorides. First a spot of a 20% sodium hydroxide solution saturated with sodium sulfite was applied to a marked position on the starting line. This was dried and a spot of the solution of sulfonylchloride (or the mixture of sulfonylchlorides) was superimposed on it. By holding the paper for a short time over a dish containing hot or boiling water, or by conditioning it in a humidity cabinet for an hour, the sulfonylchloride was reduced to the parent sulfinic salt. If several spots were applied they were spaced at intervals of about 5 cm. After developing and spraying the chromatogram, the characteristic spots of the sulfinic group appeared. The sulfite spot, which had a rather large area due to the high sulfite concentration, disappeared when the chromatogram was washed.

The \( R_F \)-values obtained are reported in Table 1.

Weighed amounts of a standard solution of sodium \( p \)-toluenesulfinate were applied from a capillary pipet to the chromatographic paper. If necessary the loading was increased by multiple applications, each spot being dried before repeating the application. In this way series of spots corresponding to from 0.5 to 80 \( \mu \)g of the salt was obtained. The minimum quantity detectable after developing, drying and spraying the chromatogram as previously described was found to be 4 \( \mu \)g which is equal to \( 2.4 \times 10^{-4} \) mole of sodium \( p \)-toluenesulfinic.

A quantitative estimation was carried out using the technique devised by Fisher \textit{et al.} The spots from a concentration series were circumscribed with a black pencil and copied on photographic document reflex paper or on transparent paper of uniform quality. The spots thus obtained are carefully cut out and weighed. By plotting on semi-logarithmic paper the weights of these "cut-outs" against the amounts of sulfinic salt applied on each spot, a straight calibration curve was obtained (Fig. 1), from which the content of an unknown sample could be determined.

The sulfonylchlorides could be examined in the same way provided the reduction was complete. Amounts as small as 100 \( \mu \)g could be detected without difficulty.

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