Thin-Layer Chromatography of Inorganic Ions.  
V. A Study of the Acetone-Sulphuric Acid Eluent System *

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Summary

In this paper we present a study of the acetone-sulphuric acid eluent system, in order to examine inorganic ion migration on thin layers of silica gel. According to the trend of their $R_F$ values with increasing acid percentage, ions are divided in four groups: ions showing low or zero $R_F$ values, ions of gradually increasing mobility with the acid percentage, ions migrating promptly with pure acetone or with a very low acid percentage and finally ions showing double spots. The varied behaviour is mainly explained on the basis of solubility and of differing tendencies to form anionic sulphate complexes. The study of this eluent system confirms our previous data and hypothesis, relating to HCl and HNO₃ systems.

Method: for the preparation, elution and detection on thin layers we refer to the previous work [2]. Solvent demixing has been studied by the technique published recently [5]. The percentages of H₂O and Me₂CO have been obtained by means of appropriate gas chromatographic techniques. The acid front was identified by titration with 0.01 M NaOH.

Results and Discussion

The study was systematically carried out employing acetone-0.5 M H₂SO₄ and acetone-6 M H₂SO₄ mixtures. We examined solvents with an acid content up to 10 % by volume. Greater acid concentrations give rise to considerable difficulty in elution and detection.

First of all we studied the solvent distribution on the layer. As is well known, a greater or lesser demixing occurs in the layer with eluents consisting of mixtures of several components. In this connection we obtained the results shown in Fig. 1 and 2.

Continuing our research on thin-layer chromatography of inorganic ions with eluents based on acetone and mineral acids [1, 2], we present here a study of the eluent system acetone-sulphuric acid.

Oguma and Kuroda [3] have recently examined the behaviour of some metals on thin layers of DEAE cellulose in organic solvent-sulphuric acid mixtures and Gaybakin [4] has used mixed solvents consisting of acetone-2M H₂SO₄ to separate some ions of groups VI and VII on thin layers of Al₂O₃.

Likewise for the eluent systems previously studied, we examined $R_F$ values either to discover the mechanisms of migration or to achieve separations.

Experimental

Adsorbent: Silica gel H (Merck)  
Solvents: acetone and 96 % sulphuric acid (d = 1.835) reagent grade (C. Erba-Milano)  
Ions and detection reagents: the solutions of salts and reagents were prepared as previously published [2].

* This work has been in part supported by C.N.R. of Italy
As regards the distribution of H₂O and acetone, we can assert that there is no sharp demixing of the two components. We find, in fact, only a continuous variation of composition. In the eluents with 0.5 M H₂SO₄ in particular the percentage of H₂O decreases on the layer, whereas in the eluents with 6 M H₂SO₄ it increases, with a consequent opposite trend of the percentage of acetone.

The acid front on the contrary shows sharp demixing and RF values rise with the increase of the percentage acid in the eluent. Moreover, with the same percentage acid, the RF of the acid front in 6 M H₂SO₄ is always greater than the one in 0.5 M H₂SO₄.

In spite of several experiments, it was impossible to single out the distribution of the HSO₄⁻ ion in the layer and to distinguish a possible front for it. We can only presume that, considering the high percentage of organic solvent, the equilibrium: H⁺ + SO₄²⁻ → HSO₄⁻ is greatly shifted to the right and therefore the bisulphate ion concentration is not negligible.

The RF values for the various ions were related, in any case, to the liquid front. The values obtained with Me₂CO-0.5 M H₂SO₄ and Me₂CO-6 M H₂SO₄ are shown in Fig. 3.

**Acetone-6 M H₂SO₄**

From the data shown in Fig. 3, we notice that the ions examined can be classified according to the behaviour of the relative RF values.