

Chromatography on a column of Raney cobalt

Platinum, palladium, nickel, and other catalysts prepared from transition metals are readily poisoned by the presence of small quantities of organo-sulphur compounds, and it has been established that the sulphur compounds are chemisorbed onto the metal via the lone pair of electrons¹. On the other hand, when an organo-sulphur compound is treated with a large excess of a hydrogen-rich catalyst, such as Raney nickel, the initial chemisorption may be followed by desulphurisation². The transition metals differ in their ability to desulphurise compounds, just as they differ in their ability as hydrogenation catalysts. Cobalt, copper and iron, for example, have some activity as desulphurisation catalysts, but are much less effective than nickel³.

It therefore seemed likely that a weak catalyst could be used, under mild conditions, to chemisorb an organo-sulphur compound without effecting desulphurisation, and that this might be adapted as a chromatographic procedure for the separation of organo-sulphur compounds.

A column of Raney cobalt mixed with sand was found to be suitable for this purpose. The mixture containing the sulphur compound was applied to the column, which was then eluted with methanol. In this way, isoeugenol, geraniol, geranyl acetate and butyl acetate were readily eluted, but 2,5-dimethylthiophen and ethyl thiophen-2-carboxylate were completely retained, and were recovered only by prolonged Soxhlet extraction of the adsorbent. No desulphurisation or hydrogenation took place. In another investigation a column of Raney cobalt prepared in this way has been found useful for the separation of a mixture of dibenzothiophen and biphenyl⁴.

Preparation of Raney cobalt. A solution of sodium hydroxide (80 g) in water (300 ml) was cooled with ice and cobalt-aluminium alloy (Light's 30% Co; 65 g) added with vigorous stirring as quickly as frothing allowed. After digesting the mixture on the water bath at 100° for 1 h the supernatant liquid was decanted and the cobalt washed by decantation with water (6 × 100 ml) and twice with methanol.

Chromatography. The freshly-prepared Raney cobalt (ca. 7.5 g) was mixed with clean sand and packed into a chromatographic column (1.2 cm × 10 cm). A mixture of isoeugenol (0.5 g) and 2,5-dimethylthiophen (0.5 g) was applied to the column and eluted with methanol (a 3-ft. head of liquid was required). Evaporation of the first fraction (30 ml) gave sulphur-free isoeugenol (0.477 g). Subsequent fractions contained only trace amounts of isoeugenol and were also sulphur-free. The dimethylthiophen was subsequently recovered by Soxhlet extraction of the cobalt with methanol.

In another experiment a column of Raney cobalt retained ethyl thiophen-2-carboxylate, but allowed butyl acetate, geraniol and geranyl acetate to pass through.

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