

CHROM. 7783

Note

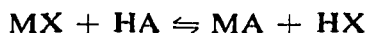
Chromatographic displacement reactions in eluents with sulphur dioxide and their application in the identification of the alkali metal ions with violuric acid and hydrogen sulphide

J. BELTRÁN-MARTINEZ and J. FAUS-PAYÁ

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valencia, Paseo al Mar 13, Valencia (Spain)

(First received April 25th, 1974; revised manuscript received July 17th, 1974)

The identification of alkali metal ions by paper chromatography with violuric acid or even with violuric acid and hydrogen sulphide^{1,2} is possible only when these ions are associated with anions of weak acids, which greatly restricts the application of this colour reagent. In order to eliminate this disadvantage, some workers³ pass the sample through an anion-exchange resin in the acetate form before carrying out the chromatography. In order to solve this problem, it would be preferable to use the chromatographic technique alone. The only possible solution is to exchange the anions of the strong acid associated initially with the alkali metal ions by suitable anions during the elution process. As the eluent must contain a weak and volatile acid¹, we thought that the anions of this acid would be suitable and then it would suffice to produce during the development the displacement reaction



where MX is the chromatographed salt and HA the acid of the eluent. This reaction seems impracticable because it involves the displacement of a weak and volatile acid (HA) for a strong acid (HX). However, we have recently shown^{4,5} that the main factors which control chromatographic displacement reactions are the relative R_F values of the four "ion pairs" involved and their relative amounts. Thus, if the R_F value of one of the products (HX generally) is greater than the R_F values of the reactants, and the amount of HA introduced by the eluent is higher, the reaction will be greatly favoured. Apparently, if HA is a weak acid, the amount of ion pairs H^+A^- will be smaller than the total amount of HA, hindering the reaction, but if the other factors are favourable the reaction will be produced substantially although HA is a weaker acid than HX.

In this work, the displacement ability for anions of strong acids in several eluents with sulphur dioxide was studied.

EXPERIMENTAL

The technique, materials and reagents were described in previous work^{1,2,4,5}.

In addition, an ethanolic solution of fuchsin (for sulphite identification) and a solution of dithizone in acetone (for zinc ions) were used.

Eluents

I. Absolute ethanol-methanol-water saturated with sulphur dioxide (70:10:20).

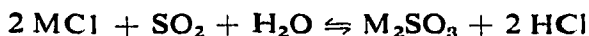
II. Absolute ethanol saturated with sulphur dioxide-water saturated with sulphur dioxide (80:20).

III. Absolute ethanol saturated with sulphur dioxide-methanol saturated with sulphur dioxide-water saturated with sulphur dioxide (50:30:20). The solvents are saturated with sulphur dioxide in an ice-bath and the elution is carried out in a refrigerator (*ca.* 5°).

IV. Absolute ethanol saturated with sulphur dioxide-aqueous 0.5 M zinc sulphite (80:20). The solution of zinc sulphite as well as the aqueous solutions of sulphur dioxide must be freshly prepared with oxygen-free water.

RESULTS

In the chromatography of alkali metal chlorides in eluents with sulphur dioxide, the displacement reactions



are favoured although sulphurous acid is weaker than hydrochloric acid because the latter has a much higher R_F value than the former (acid front of the eluent). As sodium and potassium chlorides have relatively low R_F values in the eluents used, the displacement of sulphites for chlorides is easy; for lithium chloride there is some diffi-

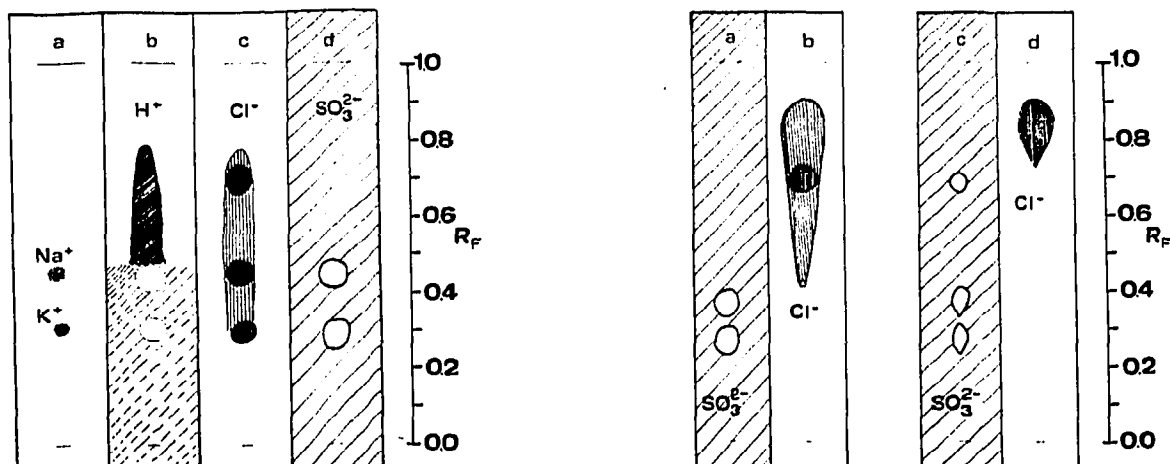


Fig. 1. Chromatography of alkali metal chlorides in eluent I. Elution at room temperature (*ca.* 20°) of 1 μ mole of each salt. Identification of (a) alkali metal ions; (b) acidity; (c) chlorides; (d) sulphites.

Fig. 2. Chromatography of alkali metal chlorides in eluent II. Elution at room temperature of 1 μ mole of each salt. Identification of (a) sulphites; (b) chlorides, 0.2 μ mole of each salt; (c) sulphites; (d) chlorides.

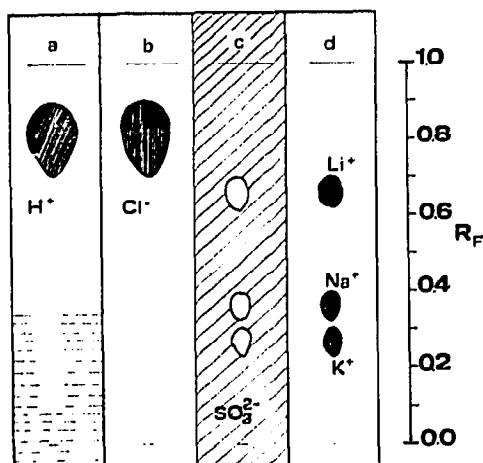
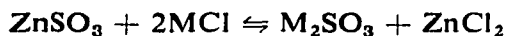


Fig. 3. Chromatography of alkali metal chlorides in eluent III. Elution at 5° of 0.5 μ mole of each salt. Identification of (a) acidity; (b) chlorides; (c) sulphites; (d) alkali metal ions.

culty because the R_F value is closer to that of hydrochloric acid and eluents with a large concentration of sulphur dioxide are needed in order to obtain satisfactory results. In Figs. 1–3 are shown the results obtained using eluents with different amounts of sulphur dioxide. The greater the amount of sulphur dioxide, the greater is the displacement ability of the eluent. Good results are obtained with eluent III up to 0.5 μ mole of each chloride (Fig. 3). After elution, the alkali metal ions are in the sulphite form, allowing their identification with violuric acid and hydrogen sulphide; all chlorides migrate as HCl. In eluents with smaller amounts of sulphur dioxide the displacements are partial (Figs. 1, 2a and 2b). However, with decreased amounts of chromatographed salts satisfactory results can be obtained because the ratio between the initial ion pairs is similarly altered⁵ (Fig. 2).

Another means of increasing the displacement ability of the eluent is to add a suitable salt to it⁵, in our case a sulphite. The nature of the cation is critical, because it is necessary that (a) the sulphite should be soluble enough in the eluent, (b) the chloride should be the fastest ion pair of the system, and (c) it should not interfere in the identification of alkali ions, giving neither a coloured violurate nor a coloured sulphide.

We studied the behaviour of several metal sulphites and found that zinc sulphite satisfied most of the above conditions. Then, in addition to displacement reactions indicated above, the reactions



are produced. The results obtained with such an eluent (eluent IV) are shown in Fig. 4. Good displacements are produced up to 1 μ mole of each chloride. The identification of alkali metal ions with violuric acid and hydrogen sulphide is satisfactory, although the spots lose their colour intensity rapidly when the paper strip is taken out of the hydrogen sulphide chamber.

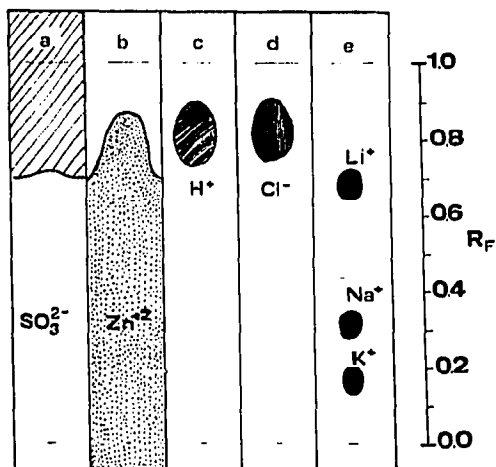


Fig. 4. Chromatography of alkali metal chlorides in eluent IV. Elution at room temperature of 0.5 μ mole of each salt. Identification of (a) sulphites; (b) zinc ions; (c) acidity; (d) chlorides; (e) alkali metal ions.

Successful results were also obtained with alkali metal nitrates using eluents III and IV, but not with sulphates; the displacement reaction is complete only for lithium sulphate and in eluent IV.

ACKNOWLEDGEMENTS

This work is part of the Doctoral Thesis of J. Faus-Payá, who thanks the Ministerio de Educación y Ciencia for the award of a research scholarship.

REFERENCES

- 1 J. Beltrán and J. Faus, *Inform. Quím. Anal.*, 26 (1972) 63.
- 2 J. Beltrán-Martinez and J. Faus-Payá, *J. Chromatogr.*, 93 (1974) 485.
- 3 H. Seiler, E. Sorkin and H. Erlenmeyer, *Helv. Chim. Acta*, 35 (1952) 120.
- 4 J. Beltrán-Martinez and J. Faus-Payá, *Rev. Acad. Cienc. Exactas, Fis.-Quím. Natur. Zaragoza*, 28 (1973) 127.
- 5 J. Beltrán-Martinez and J. Faus-Payá, *Rev. Acad. Cienc. Exactas, Fis.-Quím. Natur. Zaragoza*, 28 (1973) 327.