

Utilization of Ion Exchangers in Analytical Chemistry

XX. Separation of Ketones from Alcohols

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The aim of the present work is to study the possibility of separating ketones from alcohols with the aid of an anion exchanger saturated with bisulphite. Experiments have been performed with methanol and ethanol in the presence of acetone and methyl-ethyl-ketone.

In a previous paper it was shown that aldehydes and ketones may be quantitatively retained on passing through a column containing an anion exchanger in the bisulphite form. The adsorption is due to a formation of α -oxysulphonic acids. The aldehydes are very difficult to wash out because the aldehyde-bisulphite compounds are rather stable. Under the same conditions the alcohols are easily washed out and for that reason the aldehydes and the alcohols may be easily separated from one another by anion exchangers saturated with bisulphite¹.

For the ketones the corresponding α -oxysulphonic acids are less stable. On that account it is comparatively easy to wash out the ketones with water from an anion exchanger in the bisulphite form. Therefore, if a separation should be possible, a higher ion exchange bed must be used to achieve a separation between alcohols and ketones than for the separation of aldehydes from alcohols.

Apparatus: The ion exchanger used was Amberlite IRA-400 (particle size 0.12–0.30 mm in air-dry condition). The ion exchange columns were of ordinary type; the height of the resin layer was 550 mm and the diameter 9.8 mm. The ion exchanger was saturated with about 500 ml 1 M NaHSO₃ solution, after which it was washed with water until bisulphite could not be detected in the effluent. Because of the great filter resistance of the ion exchange resin, pressure was used in order to facilitate the passage of the solutions and the washing water through the column.

DETERMINATION OF ETHANOL AND METHANOL IN THE PRESENCE OF ACETONE

In these experiments 50 ml of a solution containing 0.5 g acetone and varying amounts of methanol or ethanol were passed through the column. Afterwards the filter layer was washed with water to give a total effluent volume of 100 ml. Washing was then continued for a further 100 ml water. Under adsorption and washing the flowrate was about 1.5–2 ml/min. In the filtrates the alcohols were determined pycnometrically. The extremely sensitive salicylaldehyde-method⁽²⁾ was used to test for the presence of acetone. The results are presented in Table 1.

As the table shows the alcohol is quantitatively recovered in the two filtrates. In these filtrates less than 0.2 per cent of the ingoing amount of acetone is found. A quantitative separation of acetone from alcohols has accordingly been achieved.

DETERMINATION OF ETHANOL IN THE PRESENCE OF METHYL-ETHYL-KETONE

In these experiments the procedure was altered in order to simplify the alcohol determination. It could be assumed that, during the passage of a mixture of alcohol and water through an ion exchange layer, the water originally present in the resin bed should be easily displaced. As no preferential adsorption between alcohol and water might be expected the concentration of the effluent should, after a short time, be the same as that of the ingoing solution.

In preliminary experiments with 2 per cent and 19 per cent ethanol in water passed through the ion exchanger and collected in fractions, it was shown that, already after 60 ml had passed, the concentration of the effluent was the same as that of the ingoing solution and that on prolonged filtration the concentration was — within the limits of experimental errors — the same (Fig. 1).

After these preliminary experiments 100 ml of water solutions with varying amounts of ethanol and 0.61 g methyl-ethyl-ketone were prepared. The solutions were passed through the layer of Amberlite IRA-400, in the bisulphite form. The first 70 ml of the effluent were discarded and then a volume, suitable for pycnometric alcohol determination, was taken. As in this case the ketone concentration in the original solution was low, the alcohol concentration of the ingoing solution may be considered the same as that of the effluent. The results presented in Table 2 show that good agreement has been obtained.

The presence of methyl-ethyl-ketone in the effluent was tested by direct spectrophotometric determination in ultra-violet light (Beckman spectro-

photometer) and by the method suggested by Thomson². By none of the methods could methyl-ethyl-ketone be detected.

The procedure applied in this section is somewhat simpler than that adopted in the previous section but may, as already pointed out, be used only if the ketone concentration is low. The accuracy for the two modifications is about the same.

Table 1.

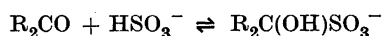
A d d e d g			F o u n d g			
Ethanol	Methanol	Acetone	Filtrate No.	Ethanol	Methanol	Acetone
0.50	—	0.50	1	0.48	—	< 0.0005
			2	0.02	—	< 0.0005
			1 + 2	0.50		
0.45	—	0.50	1	0.45	—	< 0.0005
			2	0.00	—	< 0.0005
			1 + 2	0.45		
2.00	—	0.50	1	1.97	—	< 0.0005
			2	0.04	—	< 0.0005
			1 + 2	2.01		
5.08	—	0.50	1	5.05	—	< 0.0005
			2	0.03	—	< 0.0005
			1 + 2	5.08		
—	0.50	0.50	1	—	0.50	< 0.0005
			2	—	0.00	< 0.0005
			1 + 2	—	0.50	
—	2.00	0.50	1	—	1.93	< 0.0005
			2	—	0.06	< 0.0005
			1 + 2	—	1.99	
—	5.20	0.50	1	—	5.08	< 0.0005
			2	—	0.10	< 0.0005
			1 + 2	—	5.18	

Table 2.

A d d e d g/100 ml		F o u n d g/100 ml	
ethanol	methyl-ethyl-ketone	ethanol	methyl-ethyl-ketone
0.52	0.61	0.52	< 0.003
2.06	0.61	2.05	< 0.003
5.06	0.61	5.08	< 0.003

ELUTION OF THE KETONES

As previously shown¹ the ketones may be recovered from the column already by washing with water. In the present paper higher columns have been used and therefore large amounts of water would be required if washing was performed at room temperature. However, the equilibrium



is known to be displaced to the left for an increased temperature. Therefore it must be expected that the elution may be considerably facilitated when working at elevated temperature. This was confirmed by experiments.

In the experiments given in the present paper the elution was performed by means of water at 75° C. In order to maintain this temperature a jacketed column was used. The outlet tube was cooled by ice water in order to prevent ketone losses.

For a comparison an experiment has also been made in which elution was performed by means of a solution 0.15 *M* in respect to NaHCO₃ and 0.075 *M* in respect to Na₂CO₃. This solution had in the previous investigations (1) proved satisfactory for elution of furfural.

The flow rate was kept constant in all experiments at 2 ml/min. The filtrate was taken up in fractions of 25 ml. Acetone was determined according to Thomson² and with *o*-nitrobenzaldehyde (3). When eluted with water the acetone was also determined spectrophotometrically in ultra-violet light (Beckman spectrophotometer). The latter method was also used for methyl-ethyl-ketone. Results obtained from the various analytical methods for the determination of acetone showed good mutual agreement. The results are presented in Fig. 2.

As seen from the figure methyl-ethyl-ketone is more easy to wash out with hot water than acetone. The methyl-ethyl-ketone-bisulphite compound is

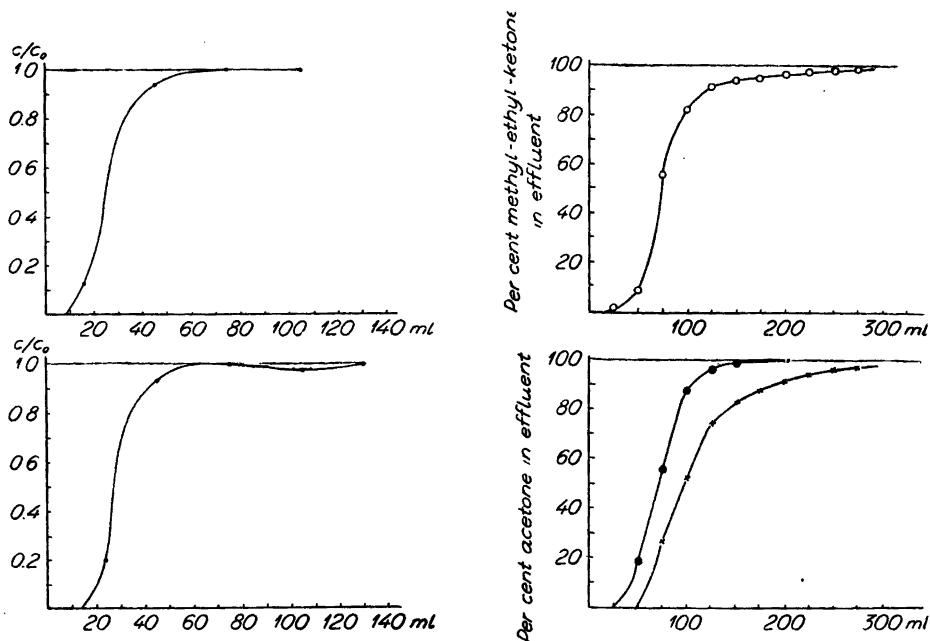


Fig. 1. Displacement of water from an anion exchange column by means of aqueous alcohol solutions.

- c = alcohol conc. in the effluent
 c_0 = alcohol conc. in the influent
 A. 2 % alcohol
 B. 19 % alcohol

Fig. 2. Integral elution curves for acetone and methyl-ethyl-ketone.

- acetone; eluant: $0.075\text{ M Na}_2\text{CO}_3 + 0.15\text{ M NaHCO}_3$
 × acetone; eluant: water 75°C
 ○ methyl-ethyl-ketone; eluant: water 75°C

evidently less stable than the acetone-bisulphite compound. This is in accordance with the behaviour of the aldehyde-bisulphite compounds, the stability of which is diminished with increasing molecular weight of the aldehydes.

With 300 ml of hot water about 99 per cent of the acetone have been eluted, whereas 99 per cent of methyl-ethyl-ketone is washed out already with 200 ml. The last traces of both acetone and methyl-ethyl-ketone are, however, difficult to wash out as the figure shows.

With the carbonate-bicarbonate solution acetone is quantitatively eluted already at about 200 ml. In this case there are no "tails" of the elution curves.

SUMMARY

Ketones can be separated quantitatively from alcohols by adsorbing the former in a column filled with an anion exchange resin in the bisulphite form.

Alcohol may be determined pycnometrically in the effluent and the ketones subsequently eluted, e.g. by means of hot water.

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REFERENCES

1. Gabrielson, G., and Samuelson, O. *Svensk Kem. Tid.* **62** (1950) 214.
2. Thomson, T. J. *Soc. Chem. Ind. (London)* **65** (1946) 121.
3. *The B. D. H. Book of Organic Reagents.* (1948) 111. The British Drug Houses LTD. Poole, Dorset.

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