

Note

Eluent conductivity suppression by thermal decarboxylation*

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Suppression of eluent conductivity in the ion chromatographic analysis of anions has been successfully accomplished using acid form cation exchange resins¹ and hollow fibre cation exchangers² with carbonate eluents. Alternative methods have been limited to electronic suppression of eluents of low ionic conductance^{3,4}.

The use of acetoacetic acid as an eluent with thermal decarboxylation to acetone and carbon dioxide has been investigated as an alternative suppressed ion chromatographic system on a quaternary ammonium bonded silica column.

EXPERIMENTAL

The chromatographic system Fig. 1 consisted of the following elements: (1) a Waters M45 pump at a flow-rate of 2 ml/min; (2) Waters U6K variable volume injector; (3) Vydac 3021C4.6 anion column 25 cm × 4.6 mm I.D.; (4) 1.5 m coil of 0.5 mm I.D. stainless-steel tubing immersed in a heated oil bath; (5) 1.5 m coil of 0.5 mm I.D. stainless-steel tubing immersed in a water bath; (6) Wescan conductivity detector Model 213A; (7) Omniscrite recorder at 0.5 cm/min; to increase the temperature obtainable in the heating coil without vapourising the eluent, a back pressure of 1500 kPa was applied to the detector outlet using a Waters U-332 union and male nut.

The acetoacetic acid was prepared by the following method; 26 g of ethyl acetoacetate was added to 12 g of potassium hydroxide previously dissolved in 400 ml of distilled deionized water. This solution was left overnight at 4°C. Aliquots of 30 ml of hydrolysed product were then washed through a column of Dowex 50W-X8 acid form resin 40 cm × 2 cm I.D. with 220 ml of distilled deionized water. The resulting 250 ml solution had a pH of 2.8 and a conductivity of approximately 2000 μ S. Atomic absorption spectroscopy was used to ensure the solution was free of potassium. Titration with 0.1 M sodium hydroxide solution gave a concentration of 50 mM as acetoacetic acid. This solution was then vacuum filtered through a Millipore 0.45- μ m filter and used as eluent.

Standards were prepared from analytical grade reagents dissolved in distilled deionized water.

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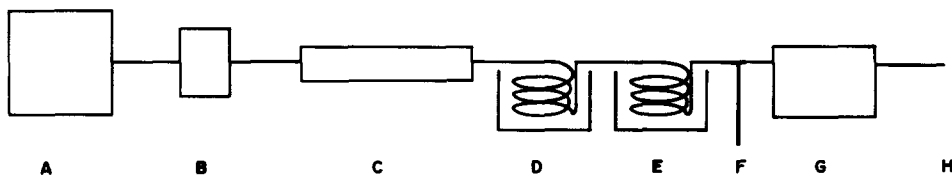
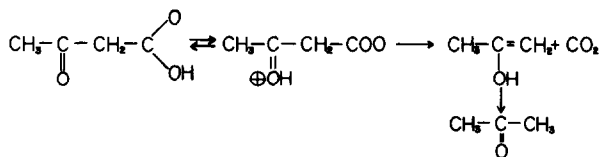


Fig. 1. Suppressed ion chromatographic system. A = Waters M45 pump, B = Waters U6K injector, C = Vydac anion column, D = heating coil (1.5 m \times 0.5 mm I.D.), E = cooling coil (1.5 m \times 0.5 mm I.D.), F = Technicon Model B₂ debubbler T, G = Wescan Model 213A conductivity detector, H = back pressure.

RESULTS

Decarboxylation of free acetoacetic acid involves transfer of the acidic hydrogen to the keto group, either prior to (as shown below) or simultaneously with loss of carbon dioxide. The decarboxylation of the anion can also occur, however the acid is probably the predominant form in a 50 mM solution as suggested by its conductivity, 2000 μ S.



Acetoacetate ion has a sufficiently low ionic conductance to be used as an eluent with electronic suppression of the eluent conductivity. In Fig. 2A a chromatogram of several anions is shown with the omission of the reaction and cooling coils from the chromatographic system. In Fig. 2B the heating and cooling coils have been added and the effects of mixing in the coils on the resolution can be considered. No observable dispersion occurs. Fig. 3 shows the effect on eluent conductivity as the temperature of the heating bath is increased to 140°C. At temperatures less than 140°C, with a flow-rate of 2 ml/min and the heating coil as described, incomplete decarboxylation of the acetoacetic acid occurred, causing the eluent conductivity to be very sensitive to variations in the heating bath temperatures. Temperatures greater than 160°C caused evolution of carbon dioxide bubbles in the eluent which did not redissolve in the ambient temperature of the cooling coil.

Attempts to debubble the eluent prior to conductometric detection by inserting a Technicon debubble T Model B₂ after the water bath were only partially successful. Considerable mixing occurred in the debubbler and back pressure applied to the debubbler waste outlet to balance that from the detector and outlet tubing had to be carefully controlled to ensure correct operation of the debubbler. Largely due to the mixing problem, it was decided to discontinue the use of the debubbler and restrict the eluent strength to 50 mM.

In Fig. 4 a chromatogram is obtained with the heating coil at 140°C. The sample and sample volume are the same as in Fig. 2 and the increase in sensitivity,

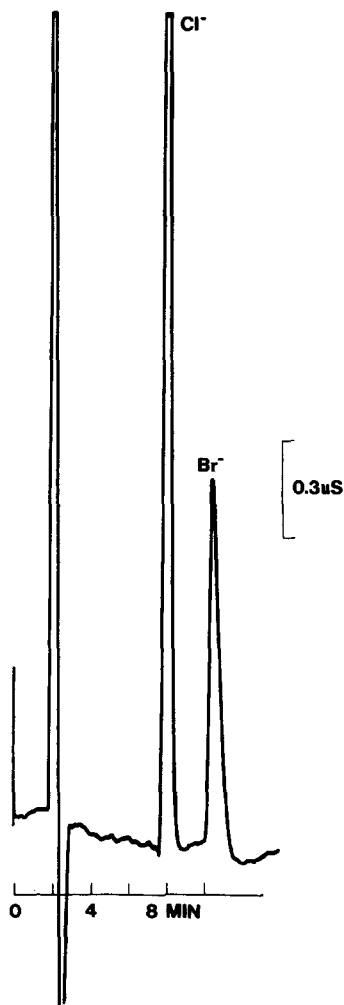


Fig. 4. Suppressed ion chromatogram with system as in Fig. 1, sample volume injected as in Fig. 2A and B and reaction coil bath at 140°C. Other conditions as in text.

approximately a factor of twenty, can be seen. This decrease is not as much as had been anticipated and the cause was identified as insufficient temperature control of the heating coil.

Acetoacetic acid solution is not a strong eluent when compared to salts of acids routinely used in ion chromatography. However it is reasonably equivalent to those acids used with a similar $\text{p}K_a$, *i.e.* phthalic acid. Unfortunately the low eluent strength, which is largely a function of the degree of ionization, restricts its use to the elution of easily eluted anions.

DISCUSSION

Thermal decarboxylation of an eluent has been shown to be an alternate method of reducing eluent conductivity prior to conductometric detection of anions. Carbon dioxide evolution and the low eluent ability of the acetoacetic acid solution are impediments to the more general applicability of this chromatographic system. The use of anions of stronger eluent ability, with potentially more attractive decomposition methods based on photochemical, electrochemical or catalytic reactions, are potential areas for further study.

REFERENCES

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