



ELSEVIER

Journal of Chromatography A, 706 (1995) 55–57

JOURNAL OF  
CHROMATOGRAPHY A

Short communication

## Colour-indication suppressor for anion chromatography

Hideki Watanabe\*, Hisakuni Sato

Laboratory of Analytical Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai 156, Hodogaya-ku, Yokohama 240, Japan

### Abstract

A background suppressor used for anion chromatography was coloured to indicate the consumption and state of regenerating of the cation exchanger. Methyl yellow and methyl red are strongly adsorbed on Dowex 50W-X8 resin. Methyl yellow is not desorbed in alkaline medium. When 0.1–0.5 ml of a 0.1% (w/w) solution of methyl yellow in methanol is added to an aqueous slurry of the resin ( $H^+$  form, 1 g) and stirred, the indicator is adsorbed quickly. The colour of the cation exchanger containing methyl yellow changes to yellow when the resin is converted from the  $H^+$  to the  $Na^+$  form with 1 mM  $NaHCO_3$  or more basic eluents. Regeneration of the suppressor column can easily be done with a 0.1–0.5 M mineral acid solution, such as HCl or  $HNO_3$ . The colour change (yellow to red-purple) indicates the completion of regeneration. One column of size  $70 \times 6$  mm I.D. has a capacity of about 3.2 mequiv., and is sufficient for 1 day of operation under the usual ion chromatographic conditions.

### 1. Introduction

Conventional ion exchangers, commercially available for preparative use, can be used as packings for suppressor columns in ion chromatography [1]. Today, membrane-type suppressors are used widely because they can be used continuously. However, column suppressors are convenient for occasional use. The most significant defect of the column suppressor is that it has a limited exchange capacity and it may become exhausted during an analysis. Therefore, it is very convenient if the remaining capacity for suppression can be established from a colour change. Miller [2] reported the use of solid indicators that involved an anion-exchange resin adsorbing pH indicators such as phenolphthalein or thymol blue. Such indicator resins can be used as the suppressor for cation chromatography. A

suppressor is thought to be more valuable for anion chromatography, in which a cation exchanger is necessary. Although a commercial coloured suppressor became available recently, the preparation method was not given [3]. In this paper, the preparation of a cation-exchange resin loaded with adsorbing pH indicators is described and its applicability is discussed.

### 2. Experimental

A pump (Tosoh, CCPM), a UV absorbance detector (Tosoh, UV-8000), a conductivity detector (Tosoh, CM-8) and a data processor (SIC Chromatocorder 11) were used. An IC anion PW separation column ( $50 \text{ mm} \times 4.6 \text{ mm}$  I.D.) from Tosoh was used. The cation exchanger used as the suppressor was Dowex 50W-X8 (200–400 mesh). Glass columns (Omni,  $70 \times 6 \text{ mm}$  I.D.) were used as the container of the coloured cation

\* Corresponding author.

exchanger. The Dowex resin was first washed with water, converted into the  $H^+$  form with 0.5 M HCl and then washed again with water.

The indicators studied were *p*-dimethylaminoazobenzene (methyl yellow), 4'-dimethylaminoazobenzene-2-carboxylic acid (methyl red) and *p*-ethoxychrysoidine hydrochloride. An aliquot of a 0.1% (w/w) solution of indicators in methanol was added to an aqueous slurry of the  $H^+$  form of cation exchanger and stirred. The coloured cation exchanger was packed into glass columns by using a glass syringe and a vacuum pump. All reagents used were of analytical-reagent grade. Water was purified with a mixed-bed ion-exchange column and with a Milli-Q system (Millipore).

### 3. Results and discussion

Relatively hydrophobic azo compounds are adsorbed very well on the  $H^+$  form of cation exchangers. Among several azo compounds, methyl yellow and *p*-ethoxychrysoidine are strongly adsorbed even in alkaline medium. Methyl red is probably desorbed in alkaline medium. The colour change of methyl yellow adsorbed on a cation exchanger takes place between pH 5 (red-purple) and 7 (yellow) and that of *p*-ethoxychrysoidine at pH 7–9. These pH values are higher than the colour change region of these indicators in aqueous solution. The colour of the cation exchanger containing methyl yellow (A) changes to yellow when the  $H^+$  ions on the exchange sites are converted into  $Na^+$  with 1 mM  $NaHCO_3$ , whereas the colour of the cation exchanger containing *p*-ethoxychrysoidine (B) does not change under the same conditions. A 1 mM borax solution changes the colour of B. As a suppressor for anion chromatography, A seems superior to B. A suitable amount of methyl yellow is about 1  $\mu\text{mol/g}$  resin. When 0.1–0.5 ml of a 0.1% solution of methyl yellow in methanol is added to an aqueous slurry of the resin ( $H^+$  form, 1 g) and stirred, all of the indicators are adsorbed quickly. A dilute solution of  $Na_2CO_3$  slowly dissolves the adsorbed methyl yellow. In a column, however, the de-

sorbed indicators are adsorbed again on the remaining  $H^+$  form of the resin. Therefore, the distribution of methyl yellow in the suppressor column shifts slowly down the column during use. If the flow direction is reversed on every regeneration with an acidic solution, the indicators do not leave the column. The boundary of the two parts,  $H^+$  form and  $Na^+$  form, can be seen clearly similarly to plug flow. Although the boundary diffuses slowly with time on storage, it soon becomes distinctive again when an alkaline eluent is passed.

Fig. 1 shows two chromatograms of a mixture of  $Br^-$  and  $NO_3^-$ . That on the left side was obtained without the suppressor and that on the right with the suppressor. Because the  $CO_3^{2-}$  and  $HCO_3^-$  in the eluent were changed to  $H_2CO_3$  by the suppressor, the background absorbance was lowered about 0.1 absorbance in the right-hand chromatogram. This effect is reflected in the intensity of the first system peaks. Baseline stability, or flatness, indicates no elution of adsorbed, coloured materials. The peaks in the right-hand chromatogram are slightly distorted by the suppressor column. If the suppressor is prepared under a higher pressure with a more pressure-safe container, the peak distortion may become smaller. The back-pressure of the present suppressor was only about 1  $\text{kg/cm}^2$ . The conductivity of the suppressed effluent was about 10  $\mu\text{S/cm}$  for the same eluent as in Fig. 1.

With the present suppressor, the detection sensitivity for nitrite ion varies depending on the

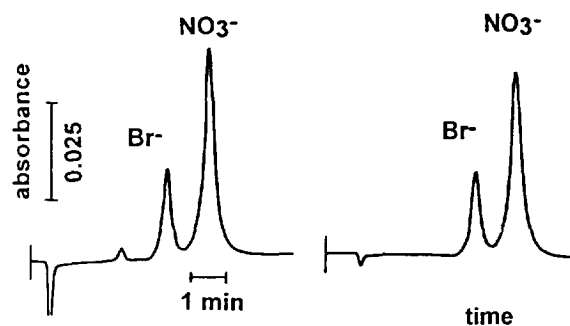


Fig. 1. Chromatograms of  $Br^-$  and  $NO_3^-$  ions without (left) and with (right) a suppressor column. Eluent, 1 mM  $NaHCO_3$ –1 mM  $Na_2CO_3$  (1 ml/min); detection, UV absorbance; sample, KBr and  $KNO_3$ , 0.1 mM each, 50  $\mu\text{l}$ .

remaining amount of the  $H^+$  form of the resin in the column, as reported [4]. To determine nitrite ion, UV absorbance detection is recommended. Because of the low back-pressure with the present suppressor column, series connection of a UV absorbance detector, a coloured suppressor column and a conductivity detector is possible. Regeneration of the suppressor column can easily be done with 0.1–0.5 M mineral acid solution, such as HCl or  $HNO_3$ . The colour change (yellow to red-purple) indicates the completion of the regeneration. The above-mentioned commercial product [3] is generally considered to be disposable.

A column of size 70 × 6 mm I.D. has a capacity of about 3.2 mequiv. and is sufficient for 1 day of operation under the usual ion chromatographic conditions. The effective time period for the continuous suppression can easily be estimated from the ion-exchange capacity, the

equivalent concentration of the eluent used and the flow-rate. Although the indicator-adsorbed cation exchanger presented here is useful as a suppressor, it is considered more convenient for the indicator to be bound covalently to the cation exchanger. Such a modification of the ion exchanger should not be difficult, and coloured exchangers may be useful in various schemes of chemical analyses for preventing erroneous operations.

### References

- [1] H. Small, T.S. Stevens and W.C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- [2] W.E. Miller, *Anal. Chem.*, 30 (1985) 1462.
- [3] R. Saari-Nordhaus and J.M. Anderson, Jr., *Am. Lab.*, 26 (1994).
- [4] W.F. Koch, *Anal. Chem.*, 51 (1979) 1571.