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Short Communication

Determination of sodium vinyl sulphonate in water-soluble polymers using capillary zone electrophoresis

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ABSTRACT

A robust capillary zone electrophoretic (CZE) method is developed for the quantitative determination of sodium vinyl sulphonate in water-soluble polymers. At the optimum concentration a precision of ± 0.26% relative standard deviation is obtained for standard solutions whereas "real samples" show a precision of ± 1.9% relative standard deviation with recoveries of 99%. The calibration is linear at least over two orders of magnitude and a detection limit of 1 mg/l is found. The CZE method is faster, more sensitive and less prone to interference than high-performance liquid chromatography and is consequently both more precise and accurate for this determination. In addition CZE is significantly more economical to perform than high-performance liquid chromatography for this analysis.

INTRODUCTION

Since the pioneering work of Jörgenson and Lukas [1] and particularly since the introduction of commercial instrumentation capillary electrophoresis (CE) has developed into a now widely accepted technique in the biomedical and related fields; however, despite the increasing number of publications few describe adequate quantitative determinations and even fewer papers concern the use of CE in industrial applications [2]. The advantages of CE such as high efficiency, small sample size and unique selectivities compared to high-performance liquid chromatography (HPLC) have frequently been discussed but the significant reduction in running costs and the avoidance of the use of large volumes of expensive and hazardous solvents also renders CE an attractive alternative to HPLC in solving problematic industrial applications.

CE has been applied by the author to the analysis of various water-soluble monomers and polymers and the present paper describes the method developed for one such product which presented difficulties for analysis by HPLC. Products based on vinyl sulphonate polymers and copolymers may be used as barium sulphate scale inhibitors, in electroplating, as powder dispersants, in photographic films and in membrane technology particularly for use in gas detectors. In researching into such polymers it is important to know the residual monomer content. Literature searches have revealed no analytical methods for the determination of sodium vinyl sulphonate in polymers.

The very polar nature of the analyte and its relatively poor UV absorbance above 205 nm together with the requirement to elute the polymer before the

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next analysis renders this a difficult determination by reversed-phase HPLC. Consequently a method based on a previous [3] publication employing a single-column ion chromatography system with conductivity detection was attempted. However this has been found to be subject to interferences from polymer components and in addition employs expensive ion-exchange columns which exhibit a short life in this application due to polymer adsorption.

As a consequence capillary zone electrophoresis was investigated and found to yield a rapid robust method with a precision equal to that expected for many HPLC methods.

EXPERIMENTS

All experiments were carried out using an ABI Model 270A electrophoresis instrument (Applied Biosystems, Warrington, UK) fitted with a Polymicro 50 μm internal diameter fused-silica capillary (Composite Metal Services, Worcester, UK) cut to a length of 50 cm, with a distance of 27 cm between the injector and detector. The capillary was washed with molar sodium hydroxide for 30 min when first prepared. The system was configured in the positive mode, *i.e.* the anode at the injection end and the capillary compartment temperature set at 30°C. For the optimum conditions the running buffer was 20 m*M* disodium tetraborate decahydrate (BDH, Poole, UK) adjusted to a pH of 8.0 using orthophosphoric acid.

The capillary was washed with a 1-min vacuum flush of 0.1 *M* sodium hydroxide followed by a 2-min flush of the running buffer between each analysis. The samples were introduced as one per cent aqueous solutions using a 2-s vacuum injection, equivalent to approximately 12 nl. A voltage of +20 kV was applied, normally for 8 min, generating a current of approximately 50 μA. The analytes were detected by the UV detector at 190 nm and the data were collected and quantified using a Waters Millipore 860, VAX-based multitasking, multi-user data system.

RESULTS AND DISCUSSION

Sodium vinyl sulphonate was found to give a good peak shape with an adequate migration of less than 6 min employing borate buffer at pH 8.0 (see Fig. 1). The net migration of the vinyl sulphonate anion is towards the cathode due to the high electroosmotic flow at this pH. The analyte ion was separated from the polymer components most of which require considerably longer than 10 min to emerge (see Fig. 2); however, for quantitative determination of the vinyl sulphonate this is not necessary as after detection of the analyte during an 8-min run the polymer is removed from the capillary by a vacuum flush before the next run.

Changes in the pH of the buffer had only a marginal effect on the migration time but the peak showed marked fronting at pH 8.5, indicating an increased differential between the migration velocity of the analyte and the electrolyte. The efficiency was slightly better at pH 7.25 than pH 8.0 but a baseline rise seen in some polymer samples was greater at this pH, therefore pH 8.0 was considered optimum. Varying the ionic strength of the buffer at a constant pH of 8.0 had little effect on the peak shape or efficiency though the migration time increased from 4.9 to 6.4 min for a change of from 15 to 25 m*M* borate.

An exceptional increase in UV absorption was observed, from a barely detectable peak at 210 nm for a 0.05% vinyl sulphonate solution to a 70-fold increase in sensitivity at 190 nm.

The baseline noise is only marginally worse at 190 nm than at 210 nm. This is in contrast to HPLC where the noise increases considerably at the lower wavelengths and where organic solvents are required the very low wavelengths become unusable. This is important for the analysis of aliphatic materials and in part compensates for the generally poorer concentration sensitivity of electrophoresis as compared to HPLC, due to the inability to inject large sample volumes.

Linearity was tested by eight repeat injections of vinyl sulphonate solutions at six concentration levels. The precision obtained for this calibration is shown in Table I. The calibration has a linear regression coefficient of 1.0000 over a 200-fold concentration range at least from 0.001 to 0.2% of vinyl sulphonate in aqueous solution which is equivalent to 0.1 to 20% in the sample. Fronting became increasingly evident at higher concentrations but this does not adversely affect the precision of measurement.

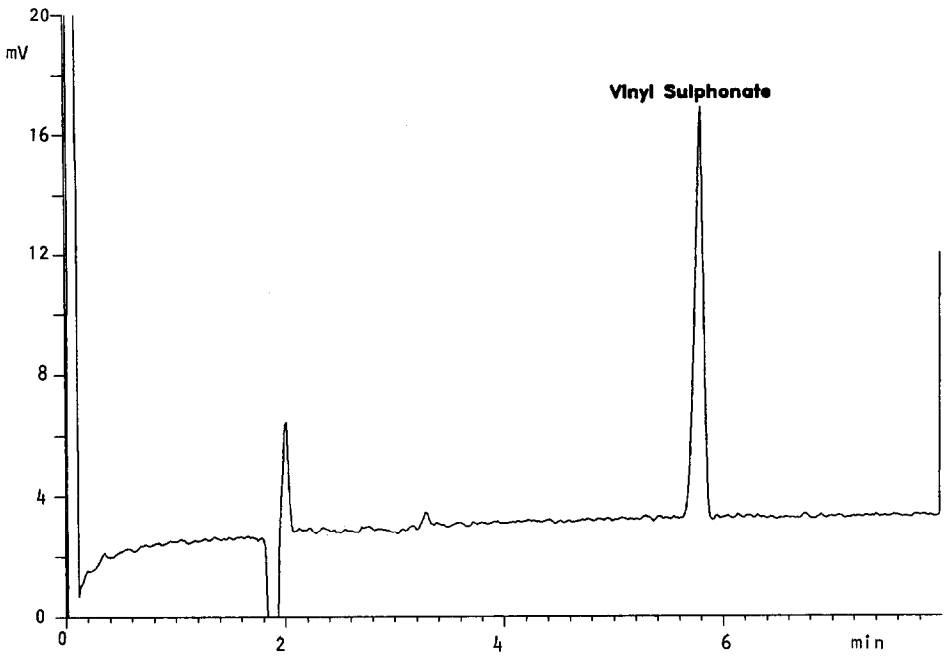

Fig. 1. Electropherogram of sodium vinyl sulphonate 0.01% aqueous solution, 2-s vacuum injection. Buffer, 20 m*M* sodium tetraborate adjusted to pH 8.0 using phosphoric acid. Applied voltage +20 kV and UV detection at 190 nm and 30°C.

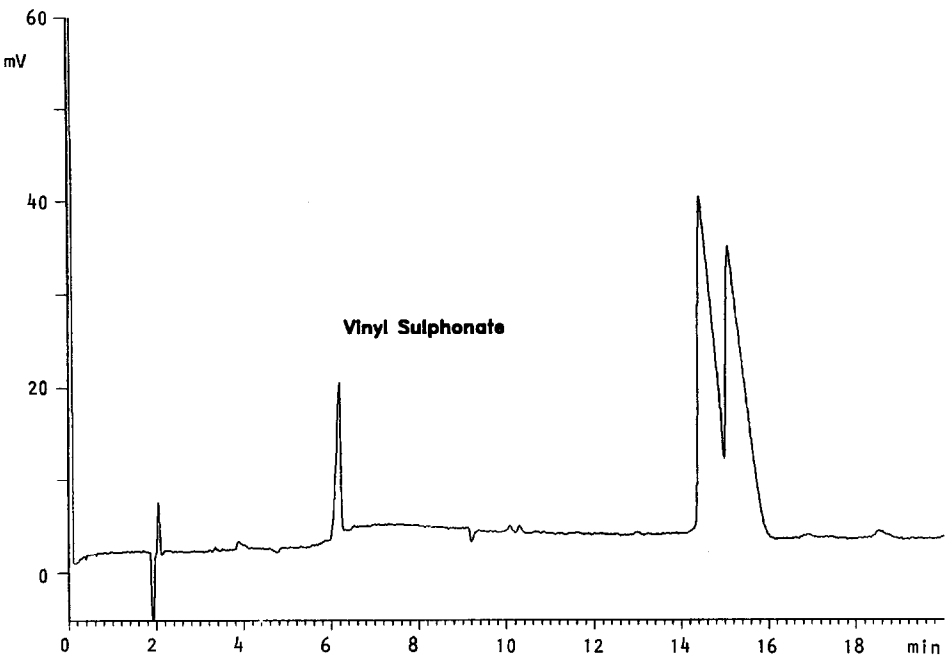

Fig. 2. Sodium vinyl sulphonate determination in a water-soluble polymer. The vinyl sulphonate level is 1.3%. Electrophoretic conditions as in Fig. 1.

TABLE I

VINYL SULPHONATE CALIBRATION, EIGHT INJECTIONS PER LEVEL

R.S.D. = Rclative standard deviation.

Vinyl sulphonate standard (%)	R.S.D. (%), migration time	R.S.D. (%), peak height	Mean number of theoretical plates	Mean response area units $\times 10^{-3}$	R.S.D. (%), peak area
0.2	0.14	0.92%	1 490	1566.07	0.26
0.1	1.04[a]	1.20%	2 860	776.53	0.54
0.05	0.28	1.16%	4 450	378.31	0.64
0.01	0.28	1.15%	16 440	76.02	0.87
0.005	0.34	0.72%	23 850	37.45	1.35
0.001	0.23	2.92%	31 410	7.86	4.49

Linear regression = 1.000, slope = 7834, intercept = −4.139

[a] Contains an outlier.

Spiking tests were carried out where levels equivalent to 0.5 and 2.5% of vinyl sulphonate were spiked into a "real" polymer sample previously found to contain no vinyl sulphonate. The recoveries over eight determinations averaged 99% for four determinations at each level.

Using the standard 2-s injection of the method the concentration limit of detection is 3 mg/l of so-

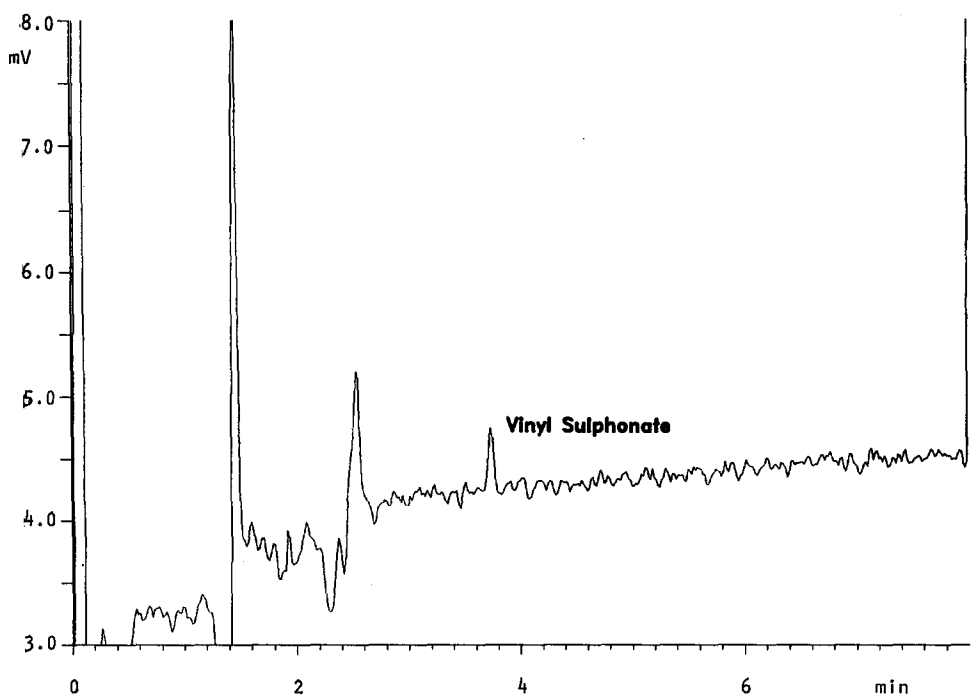

Fig. 3. Electropherogram showing limit of detection of 1 mg/l or approximately 100 fmol of sodium vinyl sulphonate in aqueous solution. Electrophoretic conditions as in Fig. 1 but 4-s vacuum injection.

dium vinyl sulphonate in aqueous solution. Using a 4-s injection the detection limit is 1 mg/l with a signal-to-noise ratio of 3:1, this is equivalent to approximately 100 fmol injected. A decrease in migration time is seen with this increased loading (see Fig. 3) and further increases in injection time are detrimental to the peak shape even for the standard alone and therefore show no gain in sensitivity. This is likely to be due to the relatively short capillary used; however, the system was optimised for speed of analysis rather than sensitivity of detection.

CONCLUSIONS

CE was found to provide a robust, precise method for the determination of residual vinyl sulphonate in water-soluble polymers which shows significant advantages over HPLC in particular yielding benefits in more accurate and economical analysis. It is likely that other ionic monomers will be equally amenable to capillary electrophoretic separation from their water-soluble polymers and that CE will become the preferred technique for their determination.

ACKNOWLEDGEMENT

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REFERENCES

1 J. W. Jorgenson and K. D. Lukas, *Anal. Chem.*, 53 (1981) 1298.
2 T. Dulffer, R. Herb, H. Herrman and U. Kobold, *Chromatographia*, 30 (1990) 675.
3 D. S. Ryder, *J. Chromatogr.*, 354 (1986) 438.