

Note

Causes for the loss of resolution in an ion chromatography resin*

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(Received March 29th, 1988)

One of the ever present facts of life for any chromatographer is that the resolution of an analytical separator column will begin to deteriorate as soon as the column is used. The lifetime of a column can be as short as a few days or weeks in the case where extremely harsh conditions are used or as long as several years of sporadic use. Two basic types of resins have been used in ion chromatography. Silica based resins are readily available but suffer the problem of limited pH range due to the degradation of silica in basic solution¹. Polymer columns do not have such strict pH limitations and have gained a wider base of use than silica columns. A common type of polymer, and the one investigated here, is a copolymer of styrene and divinylbenzene. Functional groups can then be added to the benzene ring portion of the polymer to affect ion exchange. Even with the extended stability range of the polymer columns, however, the column still has only a finite lifetime.

A cation-exchange resin which had a well documented use and which showed a marked decrease in resolution of test species was chosen for investigation in an effort to determine the mode of action whereby the resins would lose their ability to resolve species. If such a mode of action could be determined, then column cleaning procedures might be developed which would provide more effective regeneration of the column than current recommended procedures.

Resin history

The resin chosen for this work was a cation-exchange resin from a Dionex HPIC-CG2 cation-exchange column. This resin had a well documented history providing a firm foundation upon which to investigate potential mechanisms for the loss of resolution. The column had been used exclusively for the analysis of alkaline earth cations (calcium and magnesium) as well as transition metal cations from the first row transition metals. The eluants which had been used were primarily oxalic acid-citric acid mixtures with some special eluents based on lead or barium used occasionally. The samples which had been analyzed using this resin were primarily aqueous standard solutions prepared from inorganic salts or food products such as soft drinks, beer, wine, or vitamins. In addition to the above mentioned samples,

* Portions of this work were presented at the 1988 Pittsburgh Conference & Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, February 22–26, 1988, Paper No. 687.

some work was performed on acid decomposed hair samples. All of the work performed using this column was performed at room temperature.

Based on the history of the resin, four possible mechanisms for the loss of resolution were suggested. These mechanisms are: (i) polyvalent cations from the sample, the eluant, or from dissolution of stainless-steel components used occasionally with this column could be permanently bound to the resin thus effectively removing the sulfonic acid exchange sites from the exchange process, (ii) organic species from the samples could have adsorbed onto the hydrophobic portion of the resin causing some form of swelling which might lead to a decreased ability of the resin to perform its designed function, (iii) physical alterations in the physical structure of the polymer as a result of the reasonably high pressures (up to 1500 p.s.i.) under which this resin had been used might introduce physical limitations to the ion-exchange process, and (iv) chemical alterations which would chemically affect the nature of bonding within the resin thus affecting its ability to resolve target pieces. A group of experiments were designed which would test each possible mechanism and provide us the information upon which to evaluate the changes in the resin and the causes for these changes based on the history of the resin. The methods used to investigate the resin were Fourier transform infrared spectroscopy (FT-IR), solid-state nuclear magnetic resonance (NMR), inductively coupled argon plasma (ICP), scanning electron microscopy (SEM), and Schöniger flask elemental analysis for sulfur. For comparison purposes, a similar resin, unused, was taken as a blank.

EXPERIMENTAL

Inductively coupled plasma

The sample preparation procedure for the resin prior to ICP analysis involved an acid decomposition of the resin. 0.0498 g of test resin were digested in 2 ml of concentrated sulfuric acid and heated to dryness. A volume of 5 ml of aqua regia was added to the dried residue and again heated until dryness. The aqua regia decomposition was then repeated. The final residue was dissolved in 5 ml of aqua regia and diluted to 100 ml in a volumetric flask with distilled deionized water. This solution was then taken to the ICP system for analysis. After the acid digestion procedure was completed, an amount of solid equal to approximately 20% of the original resin weight was left undissolved. The solid material was felt to be of minimal significance since an amount of resin sufficient for analysis had decomposed and also, it was felt that any metals on the resin would have been extracted into the aqueous phase by the aqua regia. The ICP system used for this work was a Perkin-Elmer 5500 which has been upgraded to a Perkin Elmer 6500. The radiofrequency power was 1.25 kW with a total argon flow of 14 l/min. The sample aspiration flow-rate was 1.0 l/min. The solution was analyzed and compared to known standards for quantitative determination.

Fourier transform infrared spectroscopy

Two different experiments were performed using FT-IR. The first was to take two samples of resin, 0.030 g each, and extract one with carbon tetrachloride and the other with acetonitrile. The resin was shaken with the organic solvent and allowed to stand. The organic solvent was decanted and analyzed by FT-IR. The second

experiment involved the analysis of the solid resin by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The FT-IR system used in this work was a Nicolet 60SXB with triglycine sulfate (TGS) detector, a KBr splitter, and a Spectra-Tech DRIFTS attachment. The mirror velocity for this instrument is 0.786 cm/s. All samples reported were composites of 32 scans.

Scanning electron microscopy

Approximately 0.0002 g of resin was placed on a sample holder and gold coated. The resin was then placed in the SEM system and visual nature of the resin was characterized. The sphericity of the particles as well as the diameter of the particles were observed from the SEM images. The SEM system used in this work was a JEOL JSM T300 scanning electron microscope operated at 15 kV accelerating voltage.

Nuclear magnetic resonance

NMR was performed on the solid resin. The resin was placed in a sample holder and analyzed for a period of 8.6 h while the signal for the ^{13}C was recorded. The signal was compared to a reference and to literature values² to determine any possible changes in bonding in the resin. The NMR system used in this work was a Varian VXR 300. The spectral width was 30 000 Hz, the spin-rate was 4000 Hz, the repetition rate was 0.6 s, the line broadening was 50 Hz, the pulse sequence was CP/MAS, the number of transients was 62 000, and the observation frequency was 75 MHz.

Schöniger flask

Approximately 0.020 g of resin was wrapped in a piece of ashless filter paper and combusted in an oxygen atmosphere while being held in a platinum holder according to the directions of MacDonald³. The combustion gases were trapped in 5 ml of a trapping solution composed of distilled deionized water and four drops of 30% hydrogen peroxide. The trapping solution was then brought to a final volume of 10.0 ml in a volumetric flask and analyzed by ion chromatography to determine the total sulfur content of the resin. The sulfate in the hydrogen peroxide trapping solution was determined using a Dionex HPIC-AS4 separator column and an eluant of 0.0015 *M* sodium bicarbonate plus 0.0012 *M* sodium carbonate at a flow-rate of 1.5 ml/min. A Dionex anion fiber suppressor with 0.0125 *M* sulfuric acid regenerant was used to chemically suppress the background. The concentration of sulfate ion was determined by comparison with standards of sulfate ion prepared from the sodium sulfate salt.

DISCUSSION

Inductively coupled plasma

The results from the analysis of the used resin by acid digestion-ICP are given in Table I. The metals chosen for observation were based on one of two occurrences: (i) the metal was present in the eluent at some time during the resin lifetime, Pb and Ba, or (ii) the metal was present in samples analyzed or would be a component of the stainless-steel systems used occasionally in the lab, Cr, Ni, Mn, Fe and V. In all cases, the metals were below the detection limits of the instrument. The final column

TABLE I
DETERMINATION OF POTENTIAL BOUND METAL IONS BY ICP

Cation	Wavelength (nm)	Standard concentration (ppm)	Blank concentration*	Detection limits (ppm)	Observable mass by ICP ($\mu\text{g/g}$ resin)
Cr	205.55	10	ND	$5 \cdot 10^{-3}$	10
Pb	220.35	10	ND	$5 \cdot 10^{-5}$	0.1
Ni	231.66	10	ND	$1 \cdot 10^{-2}$	20
Mn	257.61	10	ND	$1 \cdot 10^{-3}$	2
Fe	259.94	10	ND	$3 \cdot 10^{-3}$	6
V	292.40	10	ND	$2 \cdot 10^{-4}$	0.4
Ba	455.4	10	ND	$5 \cdot 10^{-4}$	1

* ND = Not detected.

in Table I provides the amount of metal in μg metal per gram resin which should have been visible based on the stated detection limits. A rather quick calculation shows that the maximum amount of metal present, just below detection limit, would not have been sufficient to lower significantly the resolution of the column due to strong bonding with the sulfonic acid ion exchange sites.

Fourier transform infrared spectroscopy

The results of the organic extracts of the resin were inconclusive, at best. The background absorbance of the carbon tetrachloride and acetonitrile was subtracted from the samples to provide a better look at any organic signals which may have been present. The background was not subtracted completely due to the fact that there were no discernible signals present and complete subtraction of the background left only a straight line absorbance. Fig. 1 illustrates the results from the carbon tetrachloride extract with the reference resin on top and the used resin on bottom. Of most importance in this figure is the fact that there is no readily discernible difference between the two spectra. From this similarity, we concluded that there were not any large amounts of organic species adsorbed onto the surface of the resin. The second portion of the work involving FT-IR used DRIFTS to analyze the solid resin. As with the organic extracts, the experiment did not provide any positive information. The signal from the two different resins were similar and showed no meaningful difference. Fig. 2 shows the spectra of the used resin on top and that of a library spectra of polystyrene on the bottom for reference. No definitive information was obtained from this spectra.

Scanning electron microscopy

The scanning electron micrograph of the used resin is given in Fig. 3. The calculations indicate that the resin particles vary in size from $2.5 \mu\text{m}$ in diameter to $17.5 \mu\text{m}$ in size with an average diameter of approximately $10 \mu\text{m}$. This size relationship is not indicative of any significant changes in the resin; compaction due to pressure or expansion due to organic adsorption. The shape of the particles is spherical as can be seen quite easily from Fig. 3. Again, the information obtained from the SEM work was negative in that it did not elucidate the problem, only eliminated one possible mechanism.

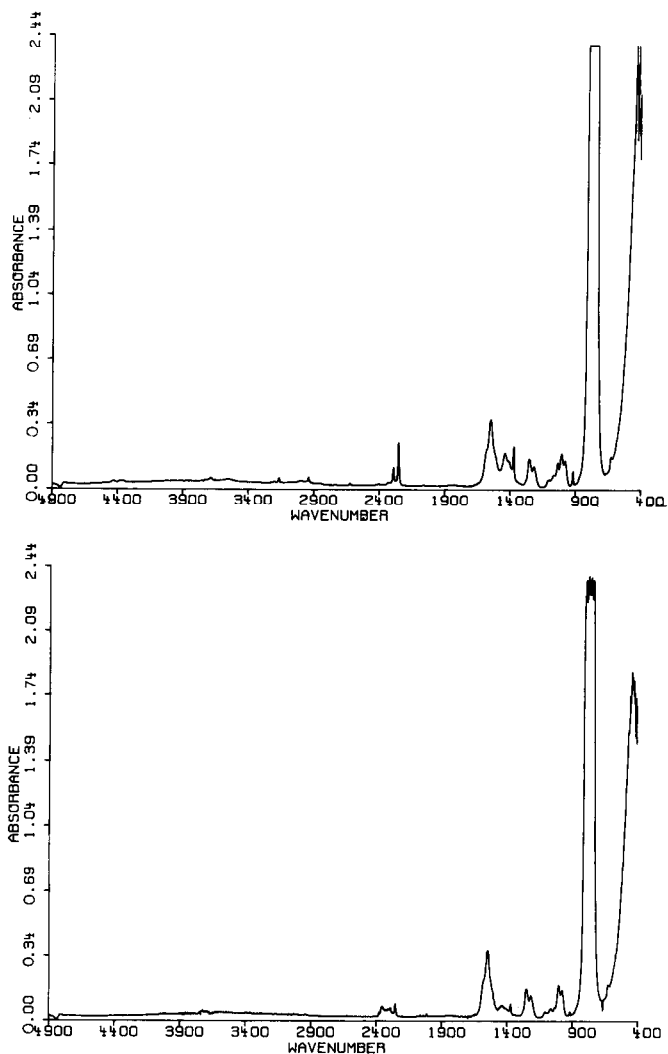


Fig. 1. Transmission FT-IR spectra from carbon tetrachloride extracts of resin. Top figure is the spectrum for the new resin and the bottom figure is for the used resin.

Nuclear magnetic resonance

NMR was the first technique to supply a clue as to the potential mechanism. The spectra obtained for the old and new resins are shown in Fig. 4, the old resin in Fig. 4A and the new resin in Fig. 4B. Again, no obvious changes which can be related to the functionality of the resin can be easily observed. Closer inspection, however, indicates that the signal from the carbon attached to the sulfonic acid group which should provide a signal at 140.39 ppm shift² is possibly decreased in the old resin. Although it is impossible to quantitate any changes from these spectra, and in fact the differences may be an artifact of the NMR itself, there did appear to be a differ-

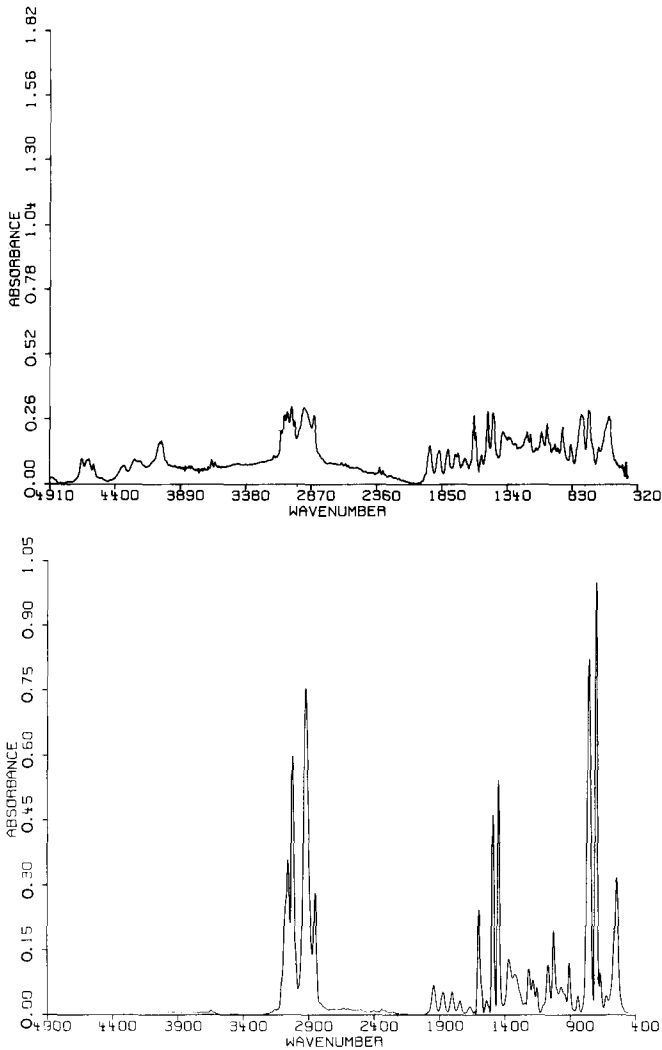


Fig. 2. DRIFTS spectra of the old resin on top and Nicolet/Aldrich Library (Volume 2, Book 3, 1593H) spectra of polystyrene on bottom.

ence in the sulfonic acid group contribution. This led us to believe that there may have been a loss in the number of sulfonic acid groups thereby leading to the possible decrease in the intensity of the carbon signal which should be attached to the sulfonic acid group.

Schöniger flask

The final experiment was done based upon the results obtained in the NMR experiment. If the sulfonic acid groups were being lost, then there should be a decrease in the total sulfur content of the resin. Elemental analysis by Schöniger flask

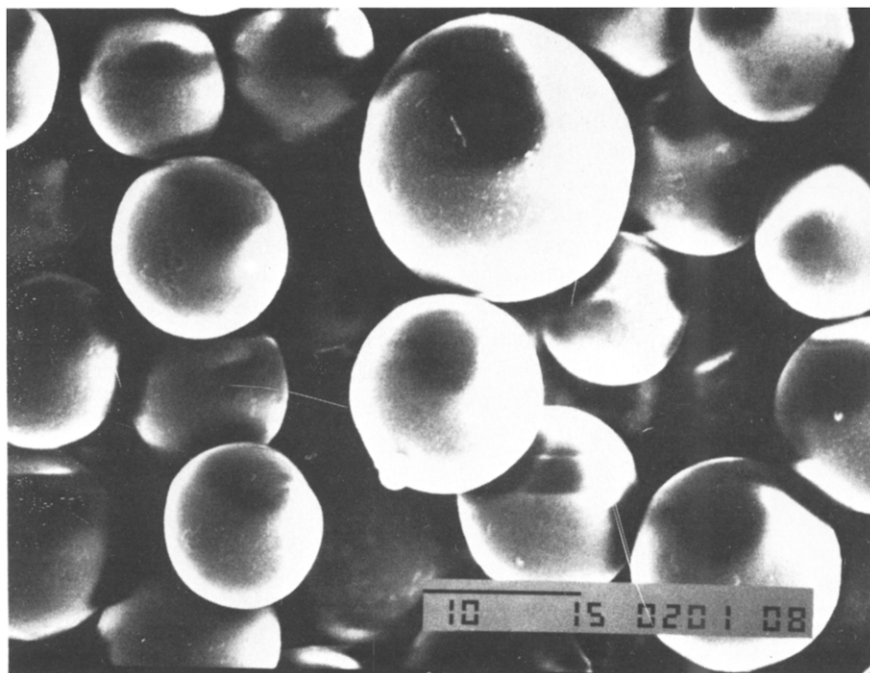


Fig. 3. Scanning electron micrograph (2000 \times) from Dionex CG2 resin.

decomposition should provide a quantitative value for the extent of loss of the sulfonic acid groups. The calculated sulfonic acid group capacity of the used resin based upon the elemental composition is 0.13 mequiv. per gram of resin. This is well below the value of the new resin. Thus the sulfonic acid groups are being lost from the resin.

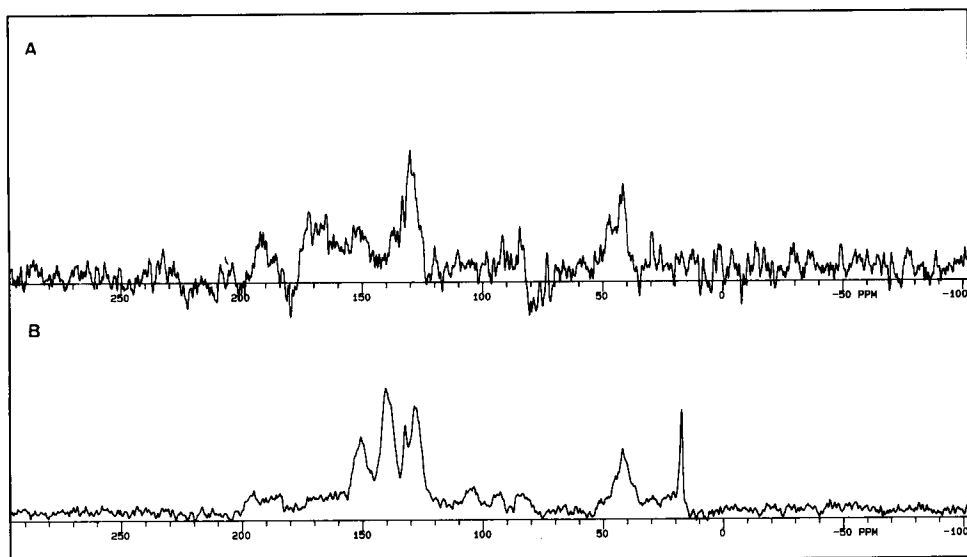


Fig. 4. Solid ^{13}C NMR spectra from (A) the old resin and (B) the new resin, bottom.

CONCLUSION

The cause for the loss of resolution, in this particular resin, was the loss of the sulfonic acid ion-exchange groups from the resin itself, thus impairing its ability to undergo sufficient ion-exchange reactions to obtain the desired resolution. The actual chemical reaction whereby the sulfonic acid group is being removed from the benzene ring has not been determined. The loss of the sulfonic acid group indicates that there would be no clean-up procedure which would help restore the resin to original specifications. Due to the nature of sulfonation of the benzene ring, resulfonation in the laboratory followed by repacking the column would not be economical due to the inconsistencies obtained in degrees of sulfonation without careful control and practice as well as the inability to repack the column to original conditions. Based upon the research described here and the conclusions drawn from that research, the loss of resolution is an irreversible process and a process which cannot be avoided.

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