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Review

The membrane suppressor: a historical perspective

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Abstract

The membrane suppressor for ion chromatography was first demonstrated in 1971. However, development of the membrane suppressor was delayed by the ease of preparation and ruggedness of a suppressor column. By 1981, a practical membrane suppressor had been developed but its excessive band broadening characteristics were not compatible with improved columns that were then being developed. The packed membrane suppressor solved the band broadening problem by 1982.

Keywords: Reviews; Ion chromatography; Membrane suppressor

Contents

1. Introduction

Eluent suppression conductimetric detection ion chromatography (IC) is the predominant chemical analysis method for the determination of common anions such as chloride and sulfate [1]. Eluent suppression conductimetric detection IC was first published in 1975 by Small et al. [2]. Eluent suppression can be accomplished by an ion-exchange reaction whereby the cations of the eluent are exchanged for: (a) regenerant cations of an ion-exchange resin packed in a suppressor column; or (b) regenerant cations of an ion-exchange membrane of a membrane suppressor [3]. The ion-exchange resin of the suppressor column is exhausted in use and is periodically regenerated. The ion-exchange membrane of the membrane suppressor can be continuously regenerated.

2. The first membrane suppressor

Small used the sequential combination of a membrane suppressor and a short suppressor column in his first demonstration of anion analysis using IC in 1971 [4]. However, the membrane suppressor tended

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to burst under the backpressure of the suppressor column and the use of a suppressor column alone provided a much more rugged and easily prepared suppressor system [4]. Our satisfaction with the suppressor column was so great and the development of the membrane suppressor was so little that we did not mention the membrane suppressor when we prepared our first publication and patent applications.

3. Development resumes

In the late 1970s, J.C. Davis joined the Analytical Laboratories of The Dow Chemical Company. He was an expert in membrane science and technology from Dow's membrane research laboratory in California, USA. He initiated a number of research projects in our laboratory using membranes in chemical analysis. When Davis approached me, I recalled Small's earlier work with the membrane suppressor. Davis and I consulted with Small and we resumed development of the membrane suppressor. We developed the membrane suppressor to the point where no auxiliary suppressor column was needed [5]. We also prepared and filed patent applications in the USA and abroad covering the membrane suppressor.

Unknown to us, Hanaoka et. al., working at a chemical analysis instrument company in Japan, had independently developed the membrane suppressor [6]. They also filed patent applications in the USA and abroad covering the membrane suppressor. However, primarily because we filed our patent applications several weeks before them, our patent applications prevailed [7].

The membrane suppressor that we had developed used a bundle of sulfonated polyethylene hollow fibers [5]. W. Rich of Dionex suggested that we use a single fiber of DuPont Nafion ion-exchange tubing. Membrane suppressors made with Nafion tubing were easier to prepare and more rugged.

The membrane suppressor was now at a stage of development where Dionex contemplated commercial introduction of a membrane suppressor using Nafion tubing. However, membrane suppressors made using Nafion tubing were not yet sufficiently developed to displace suppressor columns for many applications. The problem was band broadening. The band broadening of the membrane suppressor at this stage of its development was significantly greater than the band broadening of a suppressor column. The problem of band broadening with the membrane suppressor was made even more apparent by the development of improved columns for anion analysis by ion chromatography. I will now relate the intertwined history of the development of the improved columns and then come back to how the band broadening of the membrane suppressor was reduced to be compatible with the sharper peaks of the improved columns.

4. Improved columns

Most practitioners of IC have seen the photomicrographs of monodisperse sized ion-exchange latex agglomerated on a support [8]. However, the first IC columns were not made using such ion-exchange latex, but rather using ground ion-exchange resin [2]. The ion-exchange resin was ground and then allowed to settle in water. A colloidal suspension of relatively small ground resin particles formed over the larger particles that settled out of the colloidal suspension. The colloidal suspension was then agglomerated onto the support.

We were not satisfied with the performance of the resulting columns because the peaks of the separated ions were not well resolved. We concluded that the relatively small ground resin particles in the colloidal suspension were too small to provide sufficient ion-exchange capacity for the column and that the relatively large ground resin particles in the colloidal suspension were so large that they significantly reduced the resolution of the peaks of the separated ions.

In an effort to refine the particle size we centrifuged the colloidal suspension to settle out the larger sized fraction. Then we centrifuged the supernatant suspension at a faster speed to settle out the next smaller sized fraction and so forth until we had a number of successively smaller sized fractions. We prepared columns from each fraction. The fraction having an average particle size of about 1 μm made better columns than the larger or smaller sized fractions. Columns made using the 1 μm sized

fraction also significantly outperformed columns made using the original colloidal suspension.

Columns made using 0.6 μm sized ion-exchange latex performed even better than columns made using the 1 μm sized ground resin fraction. Columns made using 0.12 μm ion-exchange latex performed poorly just as expected from the results using similarly sized ground resin fractions. Our patent claimed an ion-exchange latex size of from 0.1 to 5 μm [9]. The 0.6 μm ion-exchange latex was used for many years as the standard of performance.

In the early 1980s I became dissatisfied with the performance of the 0.6 μm latex columns. M. Langhorst worked in the laboratory next to me and he was packing very efficient hydrodynamic chromatography columns from 15 μm Dowex 50W ion-exchange resin. My idea was to agglomerate ion-exchange latex onto these columns to obtain an improved column for IC. However, I knew that 0.6 μm latex would plug a column packed with 15 μm Dowex 50W ion-exchange resin. Therefore, I made some 0.1 μm ion-exchange latex that would not plug such a column. I hoped to gain more from the use of Langhorst's efficiently packed columns than I would loose by the use of latex of a size smaller than optimum.

To my surprise, the resulting column performed much better than expected, even when the 15 μm Dowex 50W ion-exchange resin was agglomerated with the latex in a beaker and then packed into a column. I prepared a series of ion-exchange latex of ever-smaller size and discovered that the optimum size was much smaller than 0.6 μm [10]. Our patent claimed an ion-exchange latex size of from 0.005 to 0.09 μm [11]. The use of such relatively small ion-exchange latex was also extended to porous supports [12]. These improved relatively small latex columns produced sharper peaks that were seriously degraded by the band broadening characteristics of the membrane suppressor.

5. Packed membrane suppressor

I ran a series of experiments using various ion-exchange membranes and determined that the rate-limiting step for ion-exchange in a membrane suppressor was concentration polarization of cations on the eluent side of the membrane rather than the permeability of the membrane to cations. G.L. Jewett, R.A. Bredeweg and I reviewed these results in a technical meeting and concluded that if we placed ion-exchange resin beads or just plastic beads on the eluent side of the membrane the resulting mechanical mixing caused by the beads would reduce the concentration polarization of cations on the eluent side of the membrane.

I packed beads into a membrane suppressor using Nafion tubing and determined that the length of tubing needed could be reduced by a factor of four. I packed beads into a membrane suppressor using flat Nafion membrane and determined that the area of membrane needed could also be reduced by a factor of four. We published our results [13] and obtained a patent covering the packed membrane suppressor [14].

The band broadening of an unpacked membrane suppressor was about 900 μl, a value that was unacceptable for use with the improved columns. The band broadening of the packed membrane suppressor was about 200 μl, a value that was compatible for use with the improved columns.

6. Conclusion

The membrane suppressor was first demonstrated in 1971. However, its development was delayed by the ease of preparation and ruggedness of a suppressor column. By 1981 a practical membrane suppressor had been developed but its band broadening characteristics were not compatible with the improved columns that were then being developed. The packed membrane suppressor solved the band broadening problem by 1982.

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