Journal of Chromatography, 546 (1991) 3–15
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2124

Review

Twenty years of ion chromatography

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ABSTRACT

This historical account of the development of ion chromatography traces the evolution of conductometric detection, shows how its problems created the need for new ion exchangers, describes how these materials were developed and relates how many of the innovations came from research that was unconnected to the original mission of extending chromatography to inorganic ions.

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1. INTRODUCTION

In the twenty or so years that encompass its birth and development, ion chromatography (IC) has undergone enormous changes. In its earliest embodiments IC was focused primarily on the analysis of inorganic ions; it used ion exchange to separate the ions and conductometric monitoring to detect them. Today IC has a much wider scope. It now has an important role in the analysis of organic ions as well as inorganic, it employs several separation modes besides ion exchange, and although conductometric detection is still a particularly versatile tool it is nowadays augmented with a variety of other detection methods. IC has undergone such an expansion in the past twenty years that to cover all of its aspects adequately in the alloted space and time is impossible. Fortunately, much of the task is in the capable hands of the various reviewers in the symposium so I will confine my remarks to just two topics: the evolution of conductometric detection and the development of stationary phases for IC. The technical background to these areas has received abundant discussion in many books and publications [1,2] and is by now familiar to most of the attendees. My purpose here is not to repeat much of what has already been said but rather to give an

0021-9673/91/$03.50

account of some of the historical background to the development of IC and to show how some serendipitous events played an important role. And to illustrate the tempo of development I will provide some benchmarks of progress from those early days to the present time.

2. THE EVOLUTION OF CONDUCTOMETRIC DETECTION

Those familiar with the development of chromatography will be aware that in the early seventies chromatography was firmly entrenched in organic analysis. Gas chromatography was by then a mature technique and liquid chromatography was beginning to show its great potential for those organics beyond the capabilities of gas chromatography. In contrast, the impact of chromatography in inorganic analysis was comparatively slight even though the existing methods for a great number of common and important inorganic species were often relatively insensitive, non-selective and invariably laborious and time consuming.

I had joined Dow in the Physical Research Laboratory in 1955 and during the late fifties and through the late sixties a small number of us talked frequently, and often wistfully, of extending chromatography to inorganic analysis. By the early seventies we were aware of the power of ion exchange to separate ions but recognized a major barrier to applying this in a broadly analytical way, namely, the inability in many instances to provide prompt detection of ions in the column effluent. Progress in the liquid chromatography of organic species was convenienced by their being UV absorbers in many cases. In contrast, many inorganic ions were transparent to UV and were not thought at that time to be detectable by the widely used spectrophotometers. The alkali and alkaline earth metal ions, the ammonium ion, and a great many inorganic anions such as the halides, sulfate, sulfite, nitrate, nitrite, phosphate and carbonate, etc., were just a few examples of these "problematical" ions.

One of our early attempts to solve the detection problem, while it had a very limited scope, is worth mentioning because it had an interesting sequel. In working with hydrodynamic chromatography I had become very aware of the exceptional sensitivity of spectrophotometers in detecting colloidal dispersions. So I devised a method of analysis for halides and "pseudo" halides such as thiocyanate that involved their separation by anion exchange and their photometric detection following post-column precipitation with silver nitrate. The first attempts used the high capacity anion exchanger Dowex 1 and the separation was lengthy and inefficient. Many years later when low-capacity resins became available we were able to obtain good chromatograms such as illustrated in Fig. 1. It was while doing some routine evaluation of this method for the determination of chromate ion, which is also precipitated by silver nitrate, that the idea occurred of employing chromate ion as a displacing ion in anion-exchange chromatography and using the UV detector to reveal the deficiencies in the chromate ion as non-UV-absorbing ions were eluted. This of course was the beginning of what we went on to call indirect photometric detection [3].

Besides turbidimetric detection there were other schemes that we considered from time to time but they too were usually hampered by having a rather limited range of applicability. But one property of ions that stood out as having special appeal was electrical conductivity; it was a property of all ions in solution and it was anticipated

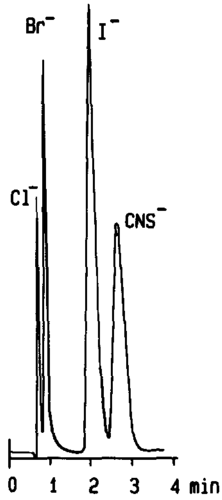

Fig. 1. Ion chromatographic separation of anions with turbidimetric detection. Stationary phase: pellicular anion-exchange resin. Eluent: 0.1 *M* sodium nitrate. Post-column precipitation with 0.01 *M* silver nitrate with gelatin. Detection: UV spectrophotometer at 280 nm.

that a conductivity detector ought to be fairly simple to fabricate and reliable in operation. But ion-exchange separation required that we use electrolytes as eluents and we were concerned that the uncertainty or noise in the very conducting background might obscure the oftentimes slight perturbations in conductivity due to the analyte species. It was to get around this problem of background noise that my colleague Bill Bauman and myself came up with the innovation that became known as "eluent suppression". For more details on the events leading up to the invention I refer readers to an earlier account [4].

The first demonstration of eluent suppression involved the separation of the three alkali metal ions lithium, sodium and potassium. It was carried out on a low-capacity cation exchanger followed by a bed of Dowex 1 in the hydroxide form to remove the hydrochloric acid eluent and convert the metal ions to their respective hydroxides. The effluent from the suppressor column, or as we called it in those days the stripper, then passed to a conductivity cell which monitored the analyte hydroxide peaks as they eluted. Fig. 2 is a photograph of this first ion chromatogram. The capacity of the separator bed was much higher than was necessary and the chromatogram took over two hours to develop but the separation was excellent, sensitivity of detection was good and we had successfully demonstrated that the concept worked. Since this is an historical account it is appropriate to mention that this occurred on November 9th, 1971.

A few days later we had demonstrated that the new technique worked also for anions (Fig. 3) but with an interesting twist in that a membrane suppressor was used to remove the sodium hydroxide eluent. Some years prior to this, while pursuing the idea of Donnan dialysis as a means of extracting magnesium out of seawater, I had developed hollow tubular cation-exchange membranes by sulfonating polyethylene surgical tubing. In the first anion separation I tried the idea of continuously

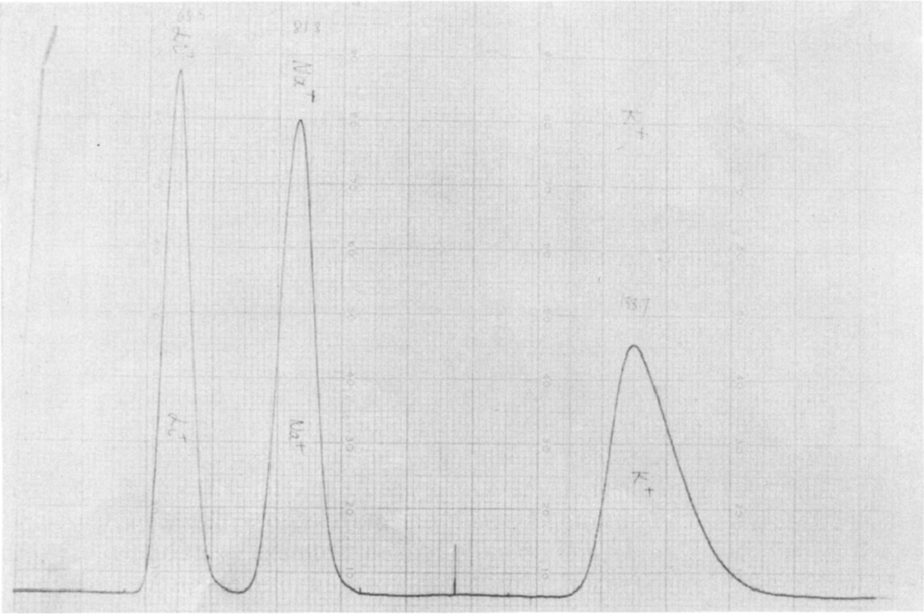

Fig. 2. First ion chromatogram using suppressed conductometric detection. Separation of cations on a surface sulfonated separator column followed by a strong base resin in the hydroxide form and conductometric detection.

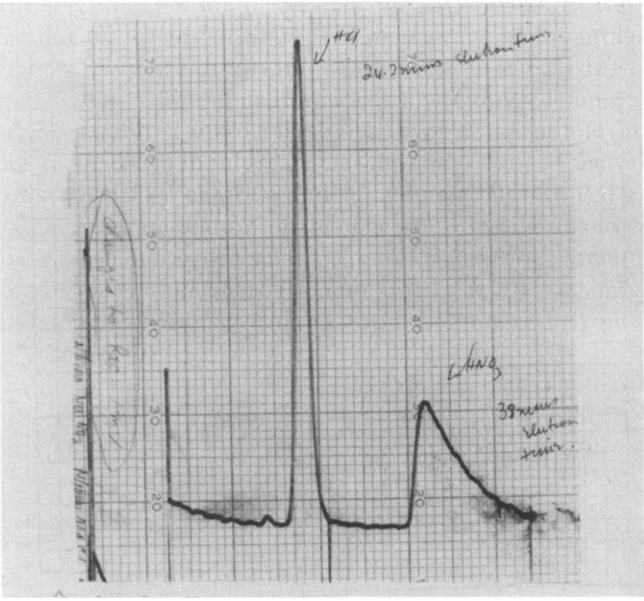

Fig. 3. First ion chromatogram of an anion separation using suppressed conductometric detection. Stationary phase: surface agglomerated anion exchanger. Tubular membrane suppressor. Conductometric detection.

suppressing eluent by allowing the effluent from the separator bed to flow down one of these sulfonated tubes that was immersed in a bath of acid. The acid was actually a stirred suspension of Dowex 50 cation-exchange resin in the hydrogen form which provided hydronium ions through "bumping" contacts with the membrane. I had considered simply using a solution of a mineral acid exterior to the tubular membrane but was concerned about acid leakage into the lumen of the fiber. This perfectly non-diffusible "solid" acid eliminated that problem. These membrane devices were very effective in removing the sodium hydroxide in anion analysis but their relatively large void volume impaired efficiency and they tended to burst under mild excess pressure. In subsequent work we used column suppressors since the resin packings were readily available, the beds were easier to prepare in a reproducible fashion and did not have the pressure limitations of the membrane devices. The idea of continuous membrane suppressors lay dormant for a time but was revived in later years when problems with column suppressors became critical [5].

Tim Stevens joined our project in early 1972 to explore the potential of the new technique for routine ion analysis. In a relatively short time Tim had achieved significant reductions in run times and had explored a variety of applications for alkali metals and ammonia analysis on some real world samples such as urine, blood serum, etc. Alkaline earth ions proved problematical for the hydronium ion based eluents and we developed the silver nitrate eluent system for these more intractable ions. Sometime around the middle of 1972 Tim had done enough to convince the analytical people that the technique had promise and he left our lab to pursue development of IC in an analytical-laboratory environment.

From the earliest tests on anion analysis it had become apparent that some major modification was necessary if one wished to extend the technique to a wide range of anions which would include those that were tightly bound to anion exchangers. For example, in these early attempts we were never able to elute anions like iodide or phosphate from the columns using sodium hydroxide as eluent. So in late 1972 we set about exploring the idea of using more potent displacing ions than hydroxide.

For an eluent to be suitable, in addition to having favorable displacing power, it had to be amenable to suppression. This considerably limited our choice but on examining a selection of ions and their anion-exchange affinity coefficients relative to the hydroxide ion, phenate looked like a good candidate. It had a high affinity and it formed a very weak acid in the suppressor. Originally we considered removing the phenol entirely by passing the effluent from the resin bed through yet another bed of charcoal but we never adopted the idea. We established elution conditions using the phenate eluent and carried out several separations that showed it to be greatly superior to the hydroxide system. It was our workhorse eluent for quite a time and was used for a great deal of anion analysis. Nowadays phenate eluents are rarely used having been displaced by the more versatile and acceptable carbonate system. Carbonate-based eluents were discovered in an interesting way.

When we were developing low-capacity resins for anion analysis we had among our tests one in which we measured the separation of chloride and bromide using sodium hydroxide as eluent. Depending on the resin's capacity, which varied over a wide range, we used one or other of two eluents —0.01 *M* and 0.05 *M* sodium hydroxide. We were bewildered at first on finding that the weaker solution was just as effective as the stronger in displacing chloride and bromide. In solving the mystery, we got our major clue when it became apparent that the 0.01 *M* solution could have become contaminated by absorbing carbon dioxide from the air while the more concentrated eluent happened to be much better protected from such contamination. The unusual potency of the more dilute eluent was proved to be due to the superior displacing power of the divalent carbonate ion that it contained. This happy accident set us on the way to a systematic study of the carbonate–bicarbonate eluent system and its eventual adoption as the eluent of choice for anion analysis by suppressed IC.

Fig. 4 represents the state of the art for anion analysis in 1975. That was a landmark year for IC; following a licensing agreement with Dow, Dionex launched its commercial development of the technique by exhibiting the first IC instrument at the fall ACS meeting in Chicago and we simultaneously published the first paper on the new technique [6]. In the years immediately following, Dionex in collaboration with its customers established the market for IC, often in areas that could not be foreseen by the original inventors. This combination of invention and marketing changed the face of inorganic ion analysis and much of organic ion analysis as well, for now instruments were available that could determine a wide diversity of ions with a speed and sensitivity that had been unattainable by the older classical methods of analysis.

As the market for IC grew, so also did alternative methods. The separation and conductometric detection of ions without the use of a suppressor was first reported in 1979 [7,8]. Subsequently, Fritz and co-workers published a series of papers and a monograph describing the new method and prescribing conditions for its application to the analysis of both cation and anion mixtures. In the non-suppressed approach, or single-column ion chromatography (SCIC) as it was originally termed, detection depends, in the first place, on their being a significant difference in conductivity between the eluting analyte ions and the prevailing eluent ions. Sensitivity of detection

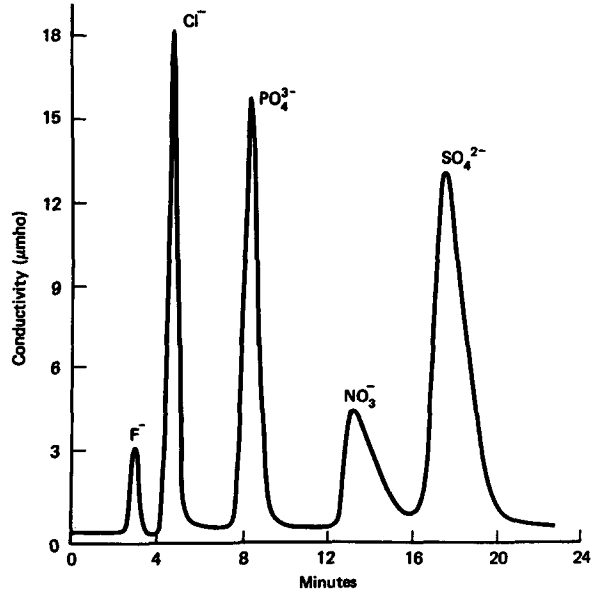

Fig. 4. Example of state-of-the-art ion chromatography *ca.* 1975.

hinges on how the perturbation of the ambient conductivity by the analyte stands out against the prevailing noise on the background conductivity. To reduce the effect of noise, the practitioners of non-suppressed IC adopted low-capacity ion exchangers and low concentration eluents. They also noted that the requirements of low eluent concentration and adequate displacing power could be more easily met if they used potent displacing ions. Organic acid ions such as benzoate, phthalate and sulfobenzoate had this property and had conductances that differed significantly from those of common inorganic analyte ions that were the focus of their interest. Choosing among the various eluents was influenced principally by the affinities of the analyte species, benzoate being preferred for mixtures such as acetate, bicarbonate, fluoride, chloride, etc. Divalent analytes and other intractable ions were more effectively eluted by phthalate or sulfobenzoate containing eluents. Analogous schemes were developed for cation analysis.

Shortly after publication of the non-suppressed approach in 1979 commercialization of the technique began, first by the Wescan Company and later by Waters, Shimadzu, Metrohm and others. At about the same time there was an evolutionary change in the meaning of the term "ion chromatography". Previously it had been applied solely to the eluent suppression technique, but with the increasing prominence of other techniques for the chromatography of ions, the name, logically, and happily, came to embrace a much wider range of methods. Nowadays the term "ion chromatography" includes any chromatographic method applied to the determination of ions.

The appearance of non-suppressed IC as well as providing an alternative way to using conductometric detection also ignited the "great debate" as to which of the two conductometric modes was the superior. For my most recent comments on the matter I refer the reader to my book on IC [1].

While column-based suppressors were employed in the earliest commercial IC instruments and many applications developed around their use, they suffered from a number of drawbacks; the interruptions to regenerate, the drifting of certain analyte peaks as the suppressor exhausted, reduced response of some species such as nitrite and the additional void volume of the second column detracted significantly from the efficiency of the newer separators. There were sufficient arguments therefore for developing an alternative means of suppression that would remove or at least minimize these undesirable effects. In the late seventies when the drawbacks of column suppressors were becoming more acute, the tubular membrane concept that had been set aside in the early days of IC was revived and developed to provide much more robust and practical devices.

The first of these new devices [5] employed a bundle of fibers in a tube and shell arrangement. They were somewhat more detrimental to efficiency than a typical column suppressor but they eliminated most of the other problems. In a later embodiment of the hollow fiber approach a single fiber was used with its lumen packed with inert polymer spheres of styrene–divinylbenzene copolymer [9]. These tiny beads essentially formed a necklace inside the lumen and led to two beneficial effects; they reduced the void volume and hence bandspreading contributed by the suppressor and they improved mass transfer within the lumen so that shorter lengths of device could supply the requisite amount of suppression. As a result of these developments, column suppressors were gradually phased out of commercial suppressed IC instruments to be replaced by both anion and cation versions of the packed hollow fiber design.

In late 1985 Dionex introduced another significant improvement in suppressor design [10]. This too was a membrane device operating under the same principles as the original, but with markedly improved suppression capacity and reduced void volume. It employed two flat membranes with effluent from the separator flowing between the membranes and regenerant flowing in the two spaces outside of the membranes. The addition of sulfonated screens to the various fluid-carrying compartments reduced void volume and enhanced mass transfer in the solution phases. The use of this low-void-volume suppressor led to notable improvements in overall efficiency but even more remarkable was its greatly improved suppression capacity, so much so that it could cope with relatively very high concentrations of sodium hydroxide and enable separations such as exemplified by Fig. 5. This is in marked contrast to the very earliest attempts to use sodium hydroxide eluents when even orthophosphate was inaccessible. This high suppression capacity also opened the door to gradient elution for the conductometric mode of IC and enabled chromatography such as is illustrated in Fig. 6.

In the continuing evolution of the suppressor technique, two very recent developments are worthy of note. Gjerde and Benson [11] have used post-separator addition of finely divided cation exchanger in the hydronium form to suppress carbonate eluents to carbonic acid. The finely divided sodium form resin particles are carried into the conductivity cell but contribute little to the overall conductivity in keeping with our understanding of the conductance of conducting particles suspended in a conducting medium [12]. In the other development, Slingsby *et al.* [13] have just recently extended the application of suppressors beyond conductometric detection. They have used a suppressor to modify eluents in order to make them more acceptable for injection into a mass spectrometer.

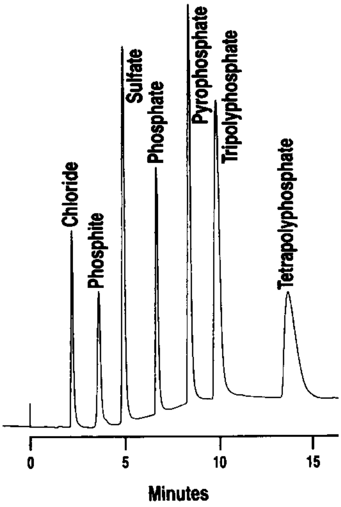

Fig. 5. Ion chromatography of anions using micromembrane suppressor. Courtesy Dionex Corporation.

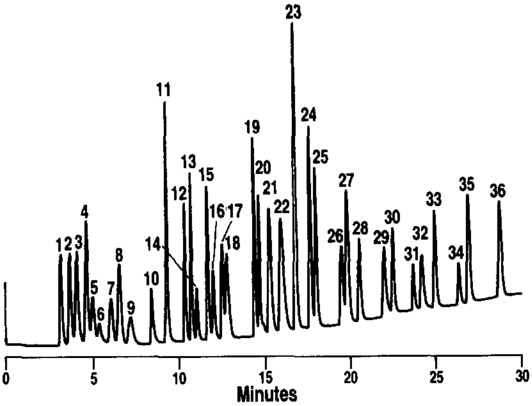

Fig. 6. Gradient elution of inorganic and organic anions on a pellicular anion-exchange resin. Eluent: gradient of 0.75 m*M* to 100 m*M* sodium hydroxide. Detection: suppressed conductometric; anion micromembrane suppressor. All anions 10 ppm unless noted otherwise. Peaks: 1 = F^- (1.5 ppm); 2 = α-hydroxybutyrate; 3 = acetate; 4 = glycolate; 5 = butyrate; 6 = gluconate; 7 = α-hydroxyvalerate; 8 = formate (5 ppm); 9 = valerate; 10 = pyruvate; 11 = monochloroacetate; 12 = BrO_3^-; 13 = Cl^- (3 ppm); 14 = galacturonate; 15 = NO_2^- (5 ppm); 16 = glucuronate; 17 = dichloroacetate; 18 = trifluoroacetate; 19 = HPO_3^{2-}; 20 = SeO_3^{2-}; 21 = Br^-; 22 = NO_3^-; 23 = SO_4^{2-}; 24 = oxalate; 25 = SeO_4^{2-}; 26 = α-ketoglutarate; 27 = fumarate; 28 = phthalate; 29 = oxalacetate; 30 = PO_4^{3-}; 31 = AsO_4^{3-}; 32 = CrO_4^{2-}; 33 = citrate; 34 = isocitrate; 35 = *cis*-aconitate; 36 = *trans*-aconitate. Courtesy Dionex Corporation.

3. STATIONARY PHASES FOR ION CHROMATOGRAPHY

Of all the elements in a chromatographic system, the stationary phase is the key. It is the stationary phase that determines what separation mechanism is operative, what the composition of the mobile phase should be and often what detection methods may be appropriately applied. Ion-exchange resins are the most widely used stationary phase in IC at the present time. They are in most cases of the low-capacity pellicular type, they are polymer based and usually derivatives of cross-linked polystyrene. This part of the article will describe how these materials were developed and show how their evolution, at least in the early stages of IC, was closely entwined with the concurrent development of conductometric detection.

When we first considered the idea of eluent suppression, we proposed a model separation of alkali metals using a system comprising a column of Dowex 50 cation-exchange resin, followed by an approximately equal-sized bed of Dowex 44, a weak base resin, and terminating in a conductivity cell. The eluent would be hydrochloric acid which the Dowex 44 would remove, leaving the analytes as peaks of metal chlorides to be conductometrically detected in a background of essentially deionized water. There was however a serious problem with this particular approach that halted progress for some time. What we were proposing to do was radical for chromatography, that is add a second bed which would exhaust during use and require replacement or regeneration. Interruptions to perform this operation could clearly become a considerable drawback if they occurred too frequently and calculation revealed that this would be the case in the first system we proposed. An alternative was to use a very large suppressor column but that solution, for obvious reasons, was out of the question. The idea that solved the problem was to use a resin in the separator with a much lower specific capacity than that in the suppressor. In this way the very small amounts of eluent required for separation would consume but a small fraction of the suppressor and permit the analysis of many samples per regeneration of the suppressor. So an early challenge in IC was how to prepare ion exchangers of requisitely low capacity.

Several years before the research on ion chromatography began, I had been exploring a concept that I called "gel–liquid extraction". It was a separation process that attempted to combine the selective chemistry of some solvent extraction systems with the superior efficiency of working in a chromatographic mode [14]. Accordingly I was swelling styrene–divinylbenzene copolymer beads with water immiscible organic extractants such as tributyl phosphate, packing them in columns and carrying out chromatographic separations using aqueous mobile phases. An aggravating property of these solvent-swollen, very hydrophobic beads was their tendency to aggregate into clusters when placed in an aqueous environment. Used in this way they packed very poorly into the columns and penalised the separation efficiency rather severely. I got around the problem by sulfonating a thin outer skin of the polymer bead leaving the mass of the core still available for swelling. Given this treatment, the beads, although swollen with solvent, gave the superficial appearance of being very hydrophilic and like an ion-exchange resin dispersed nicely when added to water. I had saved a quantity of this surface sulfonated resin from that earlier work and used it in the first cation separation (Fig. 2). Though the amount chosen was much larger than necessary, the size, capacity and crosslinking proved to be remarkably appropriate and this resin was subsequently used in a good deal of our early exploratory work.

Having demonstrated that the suppressed IC worked for cation analysis I was anxious to try the idea as soon as possible for inorganic anions for it was in this area that I anticipated it would have its greatest utility —there were other good methods, atomic absorption for example, that could be applied to inorganic cations but not to inorganic or organic anions. Anion exchangers of low capacity were available in 1971; they were being fairly widely used in high-performance liquid chromatography in conjunction with UV detectors to determine a wide range of organic ions. However, not working in an analytical laboratory I did not have immediate access to these materials and since I was very impatient to try out the idea I decided to try to prepare a resin myself. Furthermore I had doubts about the chemical stability of the commercial materials; they were based on silica and I was proposing to use them in very basic media. At first I thought of quaternizing a thin skin on the surface of the same styrene–divinylbenzene beads, analogously to the surface sulfonation procedure, but was deterred from doing this by not having any good ideas on how I might confine the ion-exchange functionality to a *sharp* surface zone (more on this point later). The solution that proved to be a very satisfactory one was again prompted by some work from many years prior on behavior that was peculiar to mixed-bed ion-exchange resins.

An old problem in mixed-bed resins was the tendency of the cation- and anion-exchange resins to clump together. It was problematical for two reasons; it gave poorly packed beds and when it was time to regenerate the resins they could be separated only with great difficulty. The experience of studying the clumping phenomenon and finding a successful means of counteracting it left me with an appreciation of the tenacious way in which cationic and anionic materials hold together, so I took substrate cation-exchange particles and exposed them to a suspension of very finely divided anion-exchange particles. The substrate particles were actually the surface sulfonated beads I had used in cation analysis —superficial functionality was all that was necessary— and the finely divided anion exchanger was some ground up IRA 400, a Rohm & Haas resin. This was the resin used in the separation of Fig. 3. Thereafter we used a variety of finely ground Dowex anion-exchange resins of various functionalities and degrees of cross-linking but eventually this proved to be an unsatisfactory and non-reproducible source of the anion-exchange material and we abandoned it in favor of the emulsion polymerization synthesis of resins. In this process, vinyl benzyl chloride and divinylbenzene are copolymerized by emulsion techniques to yield particles anywhere from 0.01 to 1 μm in diameter. These particles are then derivatised to yield anion-exchanging particles by reacting with appropriate amines at which stage they are ready for electrostatic coupling with the cation exchange substrate to form what we termed "surface-agglomerated resins".

These resins have a number of advantages over other chromatographic materials, particularly those based on silica or glass. The pellicular nature of these materials provides for excellent mass transfer properties; the electrostatic attachment of the pellicle to its substrate and the polymeric nature of both assure chemical and physical stability, particularly in the high-pH aqueous environments where silica-based materials rapidly degrade. This method of preparing pellicular resins also provides a number of advantages. The fact that the substrate and the colloidal resin are distinctly separate entities until they are agglomerated, greatly facilitates the research and development of new materials. The process provides relatively facile means for controlling those properties of the colloidal resin that impinge on the selectivity and efficiency of the final column; the functionality and cross-linking of the resin and its particle size are the most important ones. The manufacture of columns with reproducible behavior is also simplified; preparation of a large batch of colloidal resin assures that at least the chemistry of the pellicle will be the same from one column to another.

This method of preparing pellicular resins has an important advantage over the polymer-modification approach as exemplified by surface-sulfonated cation exchangers. In the latter case the boundary between the functionalized shell and the non-functionalized core is unavoidably a diffuse one. Consequently ion-exchange sites in this boundary region are not as hydrated as in the bulk of the pellicle and transport of ions in this region must necessarily be impeded. This in turn has a detrimental effect on the performance of the resins. Surface agglomerated resins do not suffer from this drawback; the outer layer of resin microparticles are uniformly swollen, the transition from functionalized to non-functionalized polymer is extremely sharp with beneficial effects on mass transfer in the pellicle region. In light of this, Dionex in recent years have applied the surface agglomeration technique to the preparation of cation exchangers thus supplanting the surface sulfonation method.

These forms of surface-agglomerated resins do have at least one drawback however; the substrate particle has a tendency to swell in organic solvents, indeed to swell a great deal in solvents with the appropriate solubility parameter. This is not a problem when aqueous eluents are used but in recent years as IC has expanded more and more into the realm of organic ion analysis where organic solvents must often be employed it has become more of a liability. It was mainly for this reason that workers at Dionex recently developed a new series of pellicular resins still using the electrostatic bonding approach but with a core that is much less susceptible to swelling. And in a very radical departure from earlier embodiments where the core is entirely inert they now involve the core as well as the pellicle in the chromatography [15]. They have done this by using macroporous polymer particles as the substrate on which to attach the ion-exchange microparticles of ion exchanger. Adding appropriate reagents, electrolytes and solvents to the mobile phase gives a hybrid form of chromatography that has components of ion-exchange and ion-pairing chromatography.

While the bulk of the research on improving resins for IC has been focused on anion analysis, there has also been significant progress in cation analysis. An interesting development in the evolution of cation exchangers has been the appearance in recent years of materials that facilitate the chromatography of alkali and alkaline earth metal ions. Surface-sulfonated, styrene-based resins permit isocratic elution of either alkali metal ions or alkaline earth ions but not of mixtures of ions from the two groups. Finding solutions to this problem has been one of the major challenges in the IC of cations and recently two successful attempts have been reported [16,17].

Kolla *et al.* [16] describe an ion exchanger prepared by copolymerizing a thin layer of butadiene and maleic acids onto a porous silica substrate. This has been applied to the isocratic separation of the more important alkali and alkaline earth metal ions using weak acid eluents and non-suppressed conductometric detection (Fig. 7). Stillian *et al.* [17] have adopted a different approach. Arguing from the basis that a resin with a lower density of sulfonated sites should display less affinity for divalent ions than a fully sulfonated version, they prepared copolymers wherein one of the monomers was comparatively inactive to sulfonation. The resulting sulfonated resins have ion-exchange sites dispersed uniformly among inert sites and enable isocratic elution of the subject ions within very acceptable time frame using suppressed conductometric detection (Fig. 8).

Although low-capacity ion exchangers for IC were initially developed as a means of getting around the various problems of conductometric detection and continue to

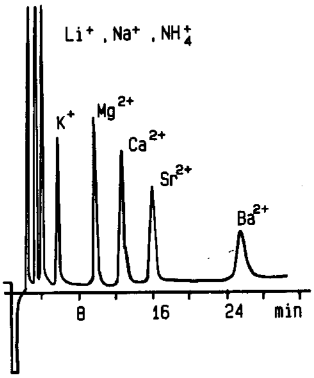

Fig. 7. Isocratic separation of alkali and alkaline earth metal ions. Stationary phase: poly(butadiene–maleic acid) on silica. Eluent: 0.01 *M* tartaric acid. Detection: non-suppressed conductometric. Ref. 16.

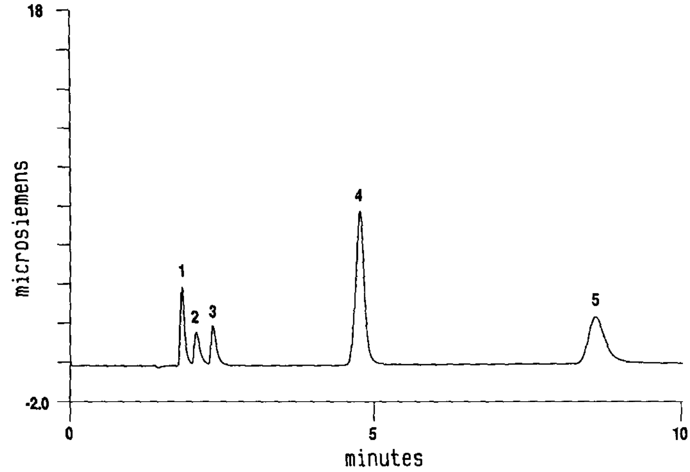

Fig. 8. Isocratic separation of alkali and alkaline earth metal ions. Stationary phase: Dionex IonPac CS10. Eluent: 60 mM HCl–6 mM diaminopropionic acid. Detection: suppressed conductometric. Peaks: 1 = sodium; 2 = ammonium; 3 = potassium; 4 = magnesium; 5 = calcium. Ref. 17.

do so, recent years have seen them being widely used with other detection modes. And capacity is no longer the only property of concern. Móre and more we see an increased understanding of resin selectivity being translated into materials with separation capabilities that are remarkably different from the early resins. We can anticipate further developments along these lines as research and development people continue to respond to the analytical challenges of ion chromatography.

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