



Evaluating eluent preparation options

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Fundamentally, chromatography requires a stationary phase and a mobile phase. Components of the analyte move between the two phases in order to be separated from each other. In ion chromatography (IC), the mobile phase is typically called the “eluent.”

Ion chromatography was originally developed with either sodium hydroxide (for anion separation) or hydrochloric acid (for cation separation) eluents (Figure 1). Hydroxide-based eluents have an advantage in that they can be suppressed to water, thereby producing a very low conductance background against which to measure the analyte response. However, challenges in eluent preparation and with suppression technology meant that carbonate/bicarbonate eluents became the standard for many years. It was only in the early 1990s that key technological developments improved the ease of use and reliability of hydroxide eluents, making them more feasible to use.

With the expanded choice of eluents for ion chromatography, it can be difficult to compare the options for eluent preparation. In this white paper we will look at the benefits and drawbacks of each. For a further exploration of the development of various methods of eluent preparation, see our educational video on Automated Eluent Generation (Figure 2).

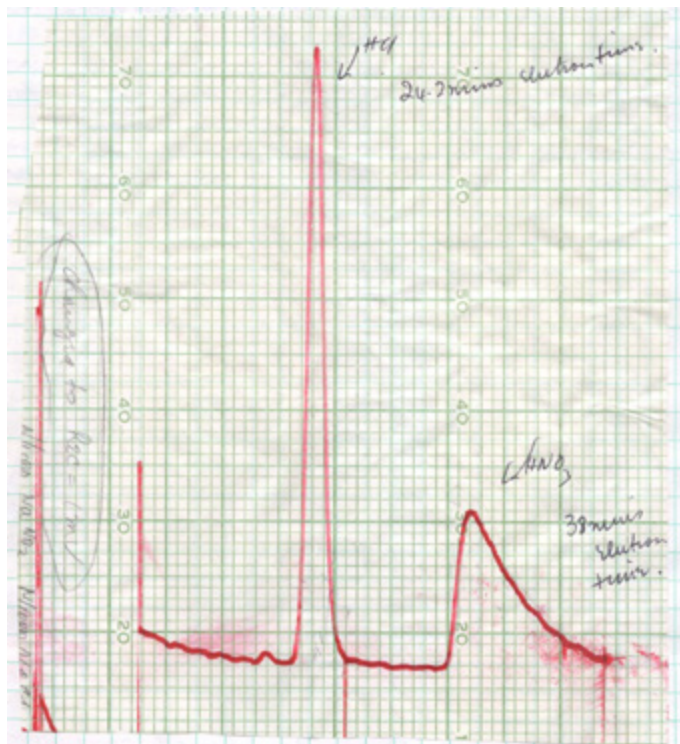


Figure 1. The first anion chromatogram using eluent suppression and conductometric detection, performed at the Dow Laboratories using NaOH eluent to separate a mixture of chloride and nitrate.
From Hamish Small's laboratory notebook, November 1971.
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Manually prepared

Eluents can be prepared manually using stock chemicals or by diluting an eluent concentrate. Either way, there is variation inherent in the eluents produced this way.

Preparation from stock chemicals

Eluents for all ion chromatography instruments can be manually prepared from stock chemicals. For eluents such as carbonate/bicarbonate, the process is straightforward. The chemicals are safe and easily available (washing soda and baking soda), and no special care needs to be taken to exclude air from the eluent.

However, there are a number of drawbacks to manual preparation from stock chemicals. The manual preparation from dry chemicals and subsequent dilutions mean that there can be considerable lot-to-lot variation in the resulting eluent concentration. Varying eluent concentrations can lead to variable retention times and issues with peak resolution.

In addition, eluents such as hydroxide and strong acids are more difficult to make manually due to safety concerns or the need to exclude air from the eluent as much as possible.



Figure 2. Click on the figure above to view a video about the evolution of eluent preparation.

Dilution of eluent concentrate

One simple way to address the variation of manual preparation is to purchase an eluent concentrate. Eluent can be prepared from this concentrate with just a single dilution.

However, only a limited number of eluent concentrates are available, restricting the eluent concentrations that can be used. (Thermo Fisher Scientific offers nine different concentrates). With less flexibility to tailor eluent concentrations, applications for these eluents are limited. Additionally, the manual dilution involved still allows the possibility of lot-to-lot variation.

Automated dilution

Automated dilution systems utilize additional components to limit the need for manual dilution (off-line automated dilution systems) and allow the ability to create eluent concentration gradients (automated eluent proportioning systems).

Off-line automated dilution

These systems typically operate by taking a measured volume of concentrate, diluting it with deionized water from a large reservoir, and filling a third bottle with eluent of the desired concentration.

Unfortunately, these systems introduce complexity to the IC system. Instead of a single eluent bottle, three bottles must be managed and kept free of contamination (Figure 3). Methods of sensing when the eluent bottle is full, or the eluent concentrate bottle is empty, currently rely on placing electrodes directly in contact with the fluid, introducing another potential source of failure or contamination. Ultimately, this method avoids a single manual dilution step in exchange for additional complexity, cost, and added sources of potential failure or contamination.

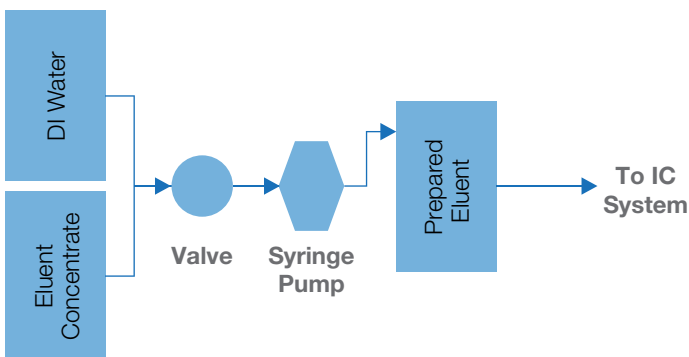


Figure 3. Automated dilution systems introduce added complexity and cost.

Automated eluent proportioning

Most IC instrument vendors offer eluent proportioning. This eluent generation technique depends upon a multi-channel valve placed immediately before the pump with inlet lines from two or more source bottles. The valve is carefully timed to allow a programmed amount of fluid from each bottle into the pump. The fluid is then mixed in a small chamber before entering the rest of the system.

Eluent proportioning offers greater flexibility because multiple source liquids can be combined at compositions that vary throughout the separation. Additionally, this technique uses only inert mechanical devices, so there are no restrictions on what type of eluents are produced. A very common application of eluent proportioning is to combine acetate and hydroxide eluents at changing concentrations for complex carbohydrate (e.g., oligosaccharide) determinations (Figure 4).

However, the technology involved in eluent proportioning can be costly and it adds complexity to setup and maintenance. Eluent proportioning is, therefore, not suitable for simple analyses.

Eluent generation

Eluent generation allows the automatic production of high-purity IC eluents. Both simple eluent generation and dual eluent generation eliminate the need to manually prepare eluents from concentrated acids and bases, requiring only deionized water as a reagent.

Simple eluent generation

Simple eluent generation produces high-purity eluents through precise control of an electric current used for the electrolysis of water to generate hydroxide and hydronium ions for anion and cation separations, respectively.

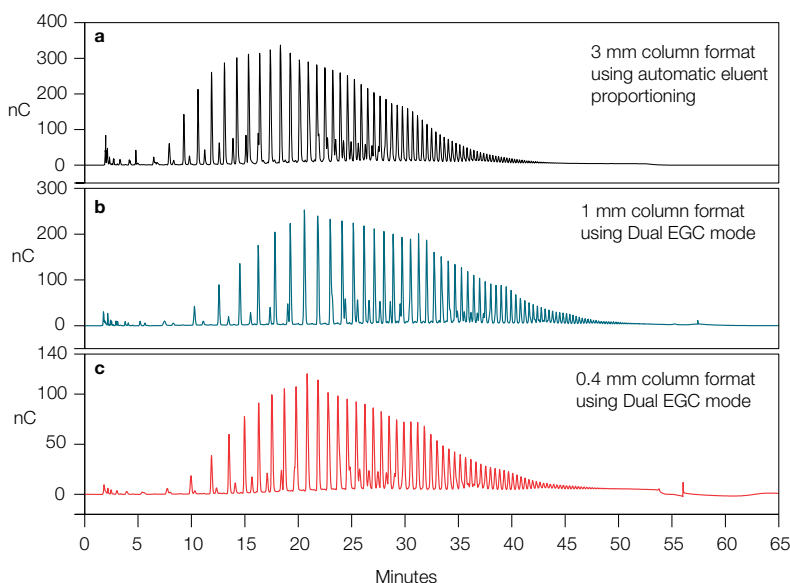
Eluent generation reduces pump maintenance because the pump seals and pistons come in contact only with deionized water, instead of acids and bases that can precipitate. Additionally, this technology enables the generation of gradients without a proportioning valve.

However, for most instruments, the practical upper limit for eluent concentration is 100 mM (hydroxide and MSA eluents). In a limited number of applications, simple eluent generation is not suitable because the analytes (e.g., oligosaccharides) are too strongly retained.

Dual eluent generation

Dual Eluent Generation places two eluent generator cartridges in series, first a methanesulfonic acid (MSA) cartridge, then a potassium hydroxide (KOH) cartridge. By balancing the concentration of the two cartridges, pure concentrations of KOH/KMSA can be generated.

Concentration gradients can be easily programmed using this eluent generation technology, allowing the replacement of manual NaOH/NaOAc gradients required for analyzing complex carbohydrates (Figure 4).



Columns: Dionex CarboPac PA200, 3 mm (guard + separator)
Dionex CarboPac PA200, 1 mm (guard + separator)
Dionex CarboPac PA200, 0.4 mm (guard + separator)

Gradient: Dionex CarboPac PA200, 3 × 250 mm
0–45 min: 100–430 mM NaOAc in 100 mM NaOH
45–50 min: 430 mM NaOAc in 100 mM NaOH
50–65 min: 100 mM NaOAc in 100 mM NaOH

Dionex CarboPac PA200, 1 × 250 mm
0–45 min: 40 mM KMSA/60 mM KOH to 156 mM KMSA/22 mM KOH
45–50 min: 156 mM KMSA/22 mM KOH
50–65 min: 40 mM KMSA/60 mM KOH

Dionex CarboPac PA200, 0.4 × 250 mm
0–45 min: 40 mM KMSA/70 mM KOH to 190 mM KMSA/10 mM KOH
45–50 min: 190 mM KMSA/10 mM KOH
50–65 min: 40 mM KMSA/70 mM KOH

Flow rate: Dionex CarboPac PA200, 3 × 250 mm: 0.5 mL/min
Dionex CarboPac PA200, 1 mm: 0.063 mL/min
Dionex CarboPac PA200, 0.4 mm: 0.010 mL/min

Detection: Dionex CarboPac PA200, 3 × 250 mm: PAD, Au on PTFE, 2 mil gasket, Ag/AgCl ref.
Dionex CarboPac PA200, 1 × 250 mm: PAD, Au on PTFE, 1 mil gasket, Ag/AgCl ref.
Dionex CarboPac PA200, 0.4 × 250 mm: PAD, Au on PTFE, 1 mil gasket, Ag/AgCl ref.

Samples: 5 mg/mL Inulin from chicory

Figure 4. Demonstration of the ability of dual eluent generation to match the separation performance of proportioned gradients, with the benefit of simplicity and reproducibility of the eluent generation solution.

Summary

Thermo Fisher Scientific offers the widest choice of eluent preparation capabilities, ensuring that you can find the most suitable solution for your application.

Eluent preparation technique		Summary	# of vendors offering	
Automated dilution	From stock chemicals	Low upfront expense, but limited application choices and subject to variation	7+	ThermoFisher Scientific
	From eluent concentrate	Simpler preparation, but many application restrictions	2	ThermoFisher Scientific
	Off-line dilution	Potentially reduced labor, but complex system and poor for gradients	2	
	Proportioning	Large application coverage, but too costly and complex for simple applications	6	ThermoFisher Scientific
Eluent Generation	Simple Eluent Generation	Just add water, but some application restrictions	1	ThermoFisher Scientific
	Dual Eluent Generation	Reagent and labor-free, not suitable for exotic applications	1	ThermoFisher Scientific

Find out more at thermofisher.com/IC

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