

The Use of Concentrator Columns in Ion Chromatography

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INTRODUCTION

Concentrator columns are short columns (typically 35–50 mm in length), which contain a stationary phase that is identical or similar to the analytical column used for the analysis. For example, a guard column is often used as the concentrator column. The function of a concentrator column is to “strip” ions from a measured volume of a relatively clean aqueous sample matrix. This process “concentrates” the desired species, which leads to lower detection limits. The advantage of using concentrator columns is the ability to perform routine analysis for ions at $\mu\text{g/L}$ (ppb) and sub- $\mu\text{g/L}$ levels without extensive and laborious sample pretreatment.

As with any trace analytical technique, the use of concentrator columns has certain limitations. For instance, at $\mu\text{g/L}$ levels the results of an analysis depend upon following laboratory practices aimed at minimizing contamination. This technical note focuses on the critical procedures to be observed when using concentrator columns, including sample handling, storage, and introduction. Proper consideration of these procedures will enable the analyst to obtain accurate and reproducible results at low $\mu\text{g/L}$ levels.

WATER QUALITY

Deionized water ($\text{DI H}_2\text{O}$) used in the preparation of eluents and standards must have a specific resistance of $17.8 \text{ M}\Omega\text{-cm}$ or better. Because $17.8 \text{ M}\Omega\text{-cm}$ resistance water can contain low $\mu\text{g/L}$ levels of ionic impurities, the quality of $\text{DI H}_2\text{O}$ with respect to ionic contamination should be determined by analyzing the water. The same ion chromatography method used for samples can be used to analyze the $\text{DI H}_2\text{O}$. To ensure that the $\text{DI H}_2\text{O}$ quality remains consistent, periodic

analysis is required. Daily analysis of a $\text{DI H}_2\text{O}$ blank is strongly recommended.

SAMPLE COLLECTION AND STORAGE

For analyses requiring $\mu\text{g/L}$ level determinations, the probability of contamination during sample collection and/or storage is high. Every container and procedural step constitutes a potential source of contamination.

Polystyrene containers with leak-tight caps can be used to store standards and samples (analyte concentrations of 1 to $10 \mu\text{g/L}$) for up to one week, provided the container was adequately flushed and soaked with $\text{DI H}_2\text{O}$ prior to use. Polystyrene tissue culture flasks (i.e., Corning orange top flasks) can also be used for sample and standard storage. Analysis of a sample storage container blank is strongly recommended.

Gloves should be worn at all times when handling samples or preparing standards.

The following procedure should be used for collection and storage of $\mu\text{g/L}$ -level samples and standards:

1. Rinse the sample container and cap 3–5 times with $\text{DI H}_2\text{O}$. Fill the container until it overflows, cap securely, and soak for four hours.
2. Empty the container and refill it with $\text{DI H}_2\text{O}$ and cap securely. Soak the container for an additional 24 hours before sample collection.
3. Empty the container and rinse it twice with the sample to be collected. Fill the container with the sample until it overflows, and cap securely. If sampling is done using a sampling line, be sure that the sample line does not touch the container.

Note: When using a sampling line, an alternate arrangement is to route the sample line directly to the ion chromatograph via a sample selection valve. This prevents batch sample contamination and eliminates the need for collection vessels.

STANDARDS

It is good practice to intersperse standards at the beginning, middle, and end of each batch of samples or more frequently to ensure reproducible instrument response. Because external calibration methods are used, it is critical that standard solutions are correctly prepared and stored.

1. Stock 1000 mg/L (ppm) standards should be prepared by accurately weighing amounts of dry salts. Salts used for standards can be dried in an oven and stored in a desiccator. Alternatively, stock standard solutions can be purchased (see Appendix A). Stock 1000 mg/L standard solutions are typically stable for two months when refrigerated.
2. Stock standards (1 mg/L) are prepared by diluting 1 mL of 1000 mg/L stock standard to 1000 mL with DI H₂O in a volumetric flask. The volumetric flask must be cleaned like a sample container. Alternatively, standards can be prepared gravimetrically, diluting 1 g into 1000 g with deionized water in the final storage container. Store the 1 ppm stock standard solutions in polystyrene containers or tissue culture flasks that have been soaked and rinsed according to the procedure outlined above.
3. Working calibration standards ($\mu\text{g/L}$) in the expected analyte concentration range, are prepared by diluting the appropriate volume of the 1 mg/L stock standard to 1000 mL with DI H₂O in a volumetric flask. Mixed working standards that contain all of the analytes of interest can be prepared. Store working standards in clean polystyrene containers. Since standard response is critical in obtaining accurate results, it is recommended that working calibration standards be prepared daily.

SAMPLE INTRODUCTION

A. Equipment Setup for Concentrator Columns

The following section describes appropriate valve (air actuated), concentrator column, and sample loop configurations that are used when concentrating analytes.

1. Configuration for a Dionex Low Pressure 4-Way Valve and concentrator column:

A Dionex Low Pressure 4-Way Valve (P/N 45008) can be used to incorporate a concentrator column in a sample injection system (see Figure 1).

In the LOAD position, the sample enters the valve at port 7 and flows out through port 8 to the concentrator column where the analytes are stripped from the matrix. The sample matrix flows out to waste via ports 4 and 3. The eluent required for the chromatographic method enters the valve at port 1 and flows through the bypass loop and to the analytical column.

In the INJECT position, the eluent is pumped through the concentrator column eluting the analytes to the analytical column where separation occurs. The sample, which may or may not be flowing depending on the method of sample loading (see *Sample Loading*, part B of this section), flows through the valve via the bypass loop and out to waste.

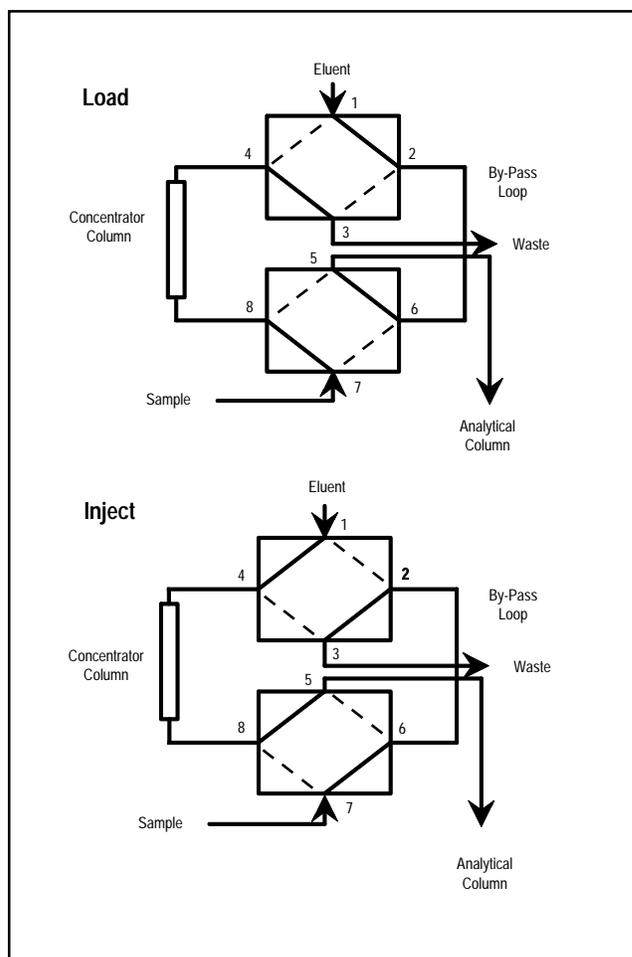


Figure 1 Configuration for a Dionex Low Pressure 4-Way Valve and a concentrator column.

It is important that the direction of sample concentration on the concentrator column and analyte elution from the concentrator column occurs in opposite directions. This setup represents an ideal configuration for concentrating a sample because the analytes are predominately retained at the end of the column that they enter first during the concentration step and then are eluted in a small volume when the valve is switched to the INJECT position.

When using a 4-way valve, a system peak prior to the water dip is observed as a result of pressure transitions when switching the valve from LOAD to INJECT and from INJECT to LOAD. The system peak typically does not interfere with the chromatographic separation.

2. Configuration for a Dionex Low Pressure 3-Way Valve and concentrator column:

A Dionex Low Pressure 3-Way Valve (P/N 45009) in conjunction with a Low Pressure 2-Way Single-Stack Valve (P/N 38754) can also be used to configure a concentrator column in a sample injection system (see Figure 2). A single air supply can be split (using a tee) to supply air to both valves simultaneously.

Using a 3-way valve minimizes the inject-to-load system peak that results when using a 4-way valve, but requires another valve (single-stack) to flush the sample lines between injections. The tubing between the 3-way and single-stack valves should be as short as possible to minimize sample carry-over. When concentrating larger sample volumes (20 mL or more), the single-stack valve can be eliminated provided that a short piece of tubing is used for sampling. The volume in a 50-cm by 0.037-inch I.D. sampling line is 350 μ L, which represents minimal sample carry-over when the total sample volume is 20 mL or greater.

The 3-way valve configuration has a flow path identical to that of the 4-way valve except that when in the INJECT position, concentrated sample is delivered to the analytical column and the incoming sample is flushed to waste through the single-stack valve.

3. Configuration for a Dionex Low Pressure 4-Way Valve and dual concentrator columns:

A Dionex Low Pressure 4-Way Valve can be used with two concentrator columns to concentrate one sample, while the previous sample is being separated on the analytical column (see Figure 3).

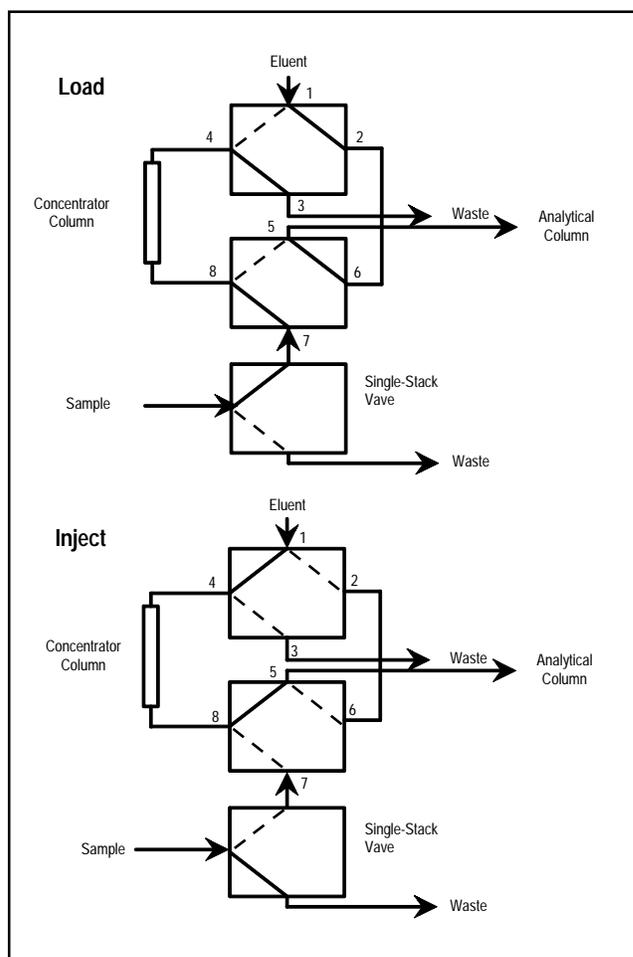


Figure 2 Configuration for a Dionex Low Pressure 3-Way Valve and a concentrator column.

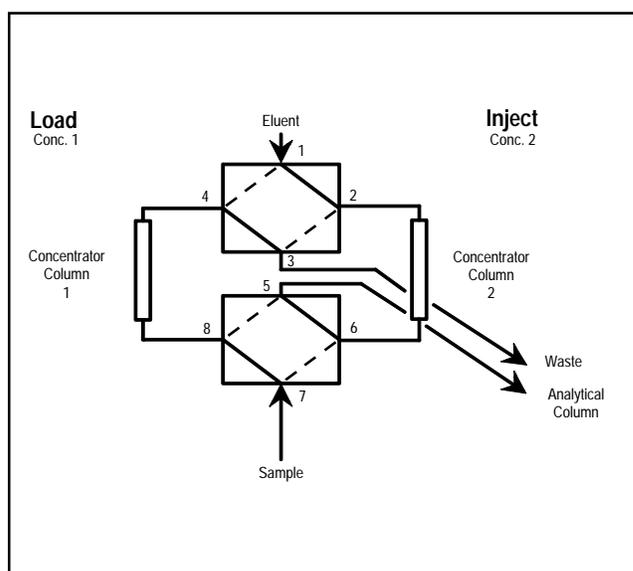


Figure 3 Configuration for a Dionex Low pressure 4-Way Valve and dual concentrator columns.

In the LOAD position, the sample is concentrated on concentrator column #1 and the eluent delivers the sample from concentrator column #2 to the analytical column. When the valve is switched, the sample is concentrated on concentrator column #2 and the eluent delivers the sample from concentrator column #1 to the analytical column.

Note: The amount of time required to concentrate the sample on the concentrator columns must be equal to or less than the chromatographic run time.

4. Configuration for a Rheodyne Valve and a concentrator column:

A Rheodyne 9126 Valve (P/N 44697) with a rotor that converts the valve from 6 ports with a needle port to a 6-port valve (valve kit P/N 45395) can be used to configure a concentrator column in a sample injection system (see Figure 4). The sample is introduced through port 6 rather than the needle port.

In the LOAD position, sample enters the valve at port 6, flows out of the valve at port 1 to the concentrator column, back into the valve through port 4, and out to waste through port 5. The eluent enters the valve at port 3 and flows to the analytical column through port 2.

In the INJECT position, the eluent is pumped into the valve at port 3 and out of the valve at port 4 to the concentrator column to elute the analytes to the analytical column. As in the previous configurations, the analytes are concentrated in one direction on the concentrator column and eluted to the analytical column in the opposite direction. The sample flow path is open to waste.

5. Configuration for a concentrator column and a sample loop:

When concentrating 10 mL of sample or less, the use of a sample loop to determine sample volume is recommended. A sample loop of a specific volume is filled with sample and then delivered to the concentrator column using water as a carrier solution (see Figure 5).

In the LOAD position (Rheodyne valve), the sample loop is filled with sample. In the INJECT position, DI H₂O pumped from an external source carries the sample from the Rheodyne valve to the Low Pressure 4-Way Valve that contains the concentrator column. (Alternatively, the system can be configured so that the Low Pressure 4-Way Valve contains the sample loop and the Rheodyne Valve contains the concentrator column).

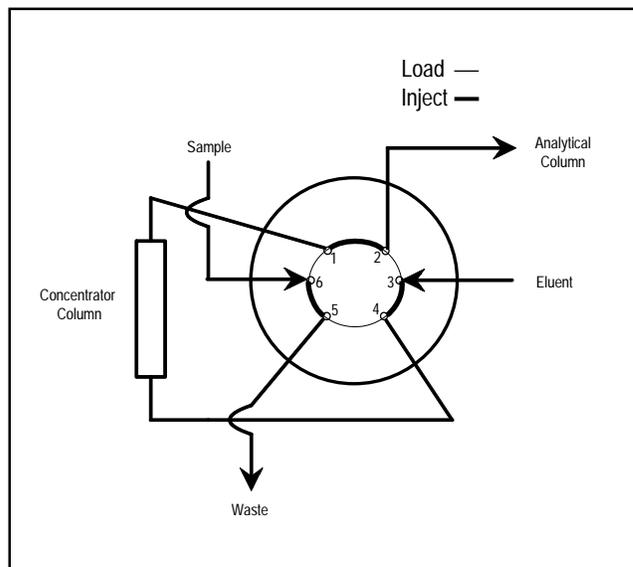


Figure 4 Configuration for a Rheodyne Valve and a concentrator column.

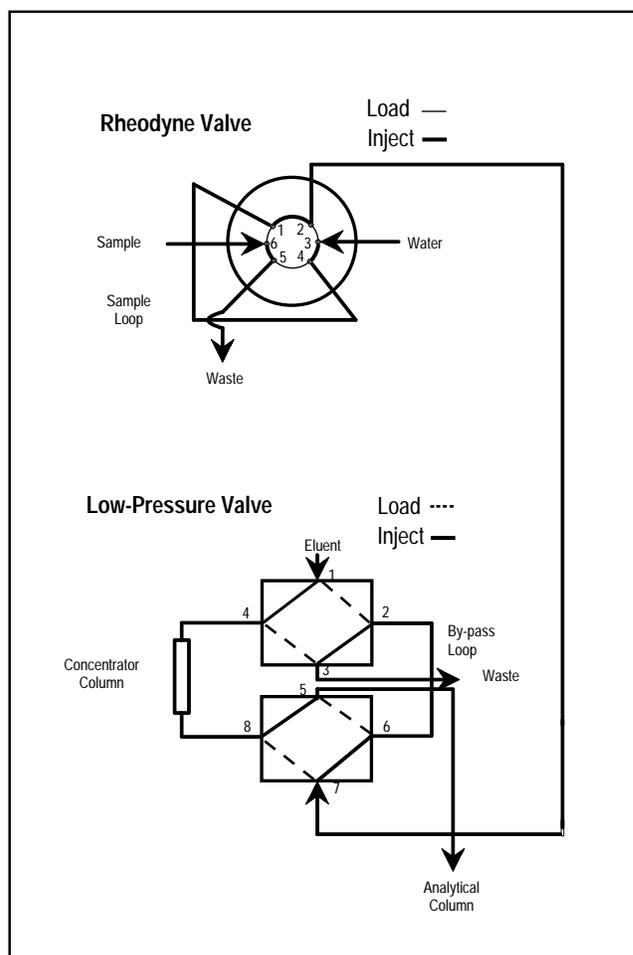


Figure 5 Configuration for a concentrator column and a sample loop.

The sample is delivered to the Low Pressure 4-Way Valve with the valve in the LOAD position so that the sample is pumped through the concentrator column and then out to waste. The analytes of interest are retained on the concentrator column and the carrier water is pumped to waste.

Sufficient water, at least three times the loop volume, is pumped through the two valves to ensure that all of the sample is delivered to the concentrator column before the Low Pressure 4-Way Valve is switched to the INJECT position. In the INJECT position, the analytes retained on the concentrator column are eluted (in the opposite direction of concentration) to the analytical column.

The use of a sample loop provides a more reproducible sample volume than using a sampling pump flow rate to determine sample volume (see *Sample Loading*, part B of this section).

Note: High-purity water, 17.8 M Ω -cm resistance or better, must be used as the carrier solution. Daily analysis of a deionized water blank is strongly recommended.

B. Sample Loading

1. Pumps

Single piston DQP (P/N 35250), DXP (P/N 43047), or Reagent (P/N 42043) pumps can be used to load concentrator columns or sample loops with sample, or pump carrier water to deliver sample from a sample loop to a concentrator column. The DQP, which has a flow rate range of 0.5 to 6.0 mL/min and a pressure limit of 13.1 MPa (1900 psi), is used for sample concentration when flow rates of 2 to 6 mL/min are required. When using microbore (2-mm I.D.) concentrator columns requiring flow rates of less than 1.0 mL/min, the Reagent Pump is used. The flow rate range and pressure limit of the Reagent Pump are 0.1 to 1.0 mL/min and 3.4 MPa (500 psi), respectively. The DXP can be used instead of a DQP provided flow rates greater than 4.0 mL/min are not required. The flow rate range and pressure limit of the DXP are 0.5 to 4.0 mL/min and 27.6 MPa (4000 psi), respectively.

A sampling pump can also be used to “pull” the sample from a sample container, through a sample loop to the pump. In this configuration, a pump is placed at the sample waste line of the valve (see Figure 5) and draws the sample into the sample loop. With this technique, the sample that is ultimately delivered to

the concentrator column does not flow through the sampling pump and a potential source of contamination, the sampling pump itself, is eliminated from the sample flow path.

Sampling pump flow rate is dependent on both system backpressure and sample pressure (if the sample is maintained under pressure). The pressure on the sampling pump must be adjusted to provide consistent flow, especially if flow rate is used to determine the sample volume to be concentrated.

When using a sampling pump in a configuration that does not include a sample loop, where the pump delivers the sample directly to a concentrator column, the reproducibility of the sampling pump flow rate must be verified. To obtain a consistent flow rate, approximately 700 kPa (100 psi) backpressure must be maintained on the pump. A convenient way to do this is to place a guard column or a backpressure regulator (P/N 39760) on the sample waste line. In addition, if the sample container is maintained under pressure, the pressure on the sample cannot result in a flow rate from the sampling pump when turned off that exceeds the desired flow rate required for concentrating the sample on the concentrator column. The sampling pump is unable to slow the flow rate to that required for the concentrator column.

2. Pressurized Sample Containers

A Pressurizable Reservoir Chamber (P/N 37053) can be used as the sample container to deliver sample to a sample loop. This eliminates the need for a sampling pump, but requires loading of a sample in the reservoir chamber.

For a 5-mL sample loop made from 0.037-inch I.D. tubing, 35 kPa (5 psi) is maintained on the reservoir and delivers sample at approximately 2 mL/min. A 7.5-min loading time fills the loop three times. This minimizes carry-over from previous samples.

3. Autosamplers

The ASM or AS40 Autosamplers can be used to load a sample loop or a low pressure concentrator column such as a TAC-LP1 or TCC-LP1. The maximum backpressure an ASM or AS40 can pump against is 700 kPa (100 psi). Sample from a series of sample vials can be loaded consecutively with either the ASM or the AS40 Autosampler.

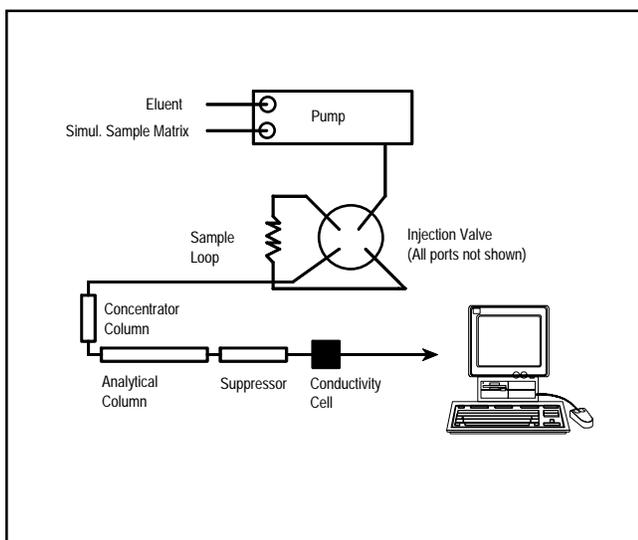


Figure 6 Configuration for breakthrough volume determination.

C. Concentrator Column Breakthrough Volume

To concentrate analytes on a concentrator column, the analytes must be present in a relatively low ionic-strength sample matrix. A high ionic-strength sample acts as an eluent and prevents retention of the analytes on a concentrator column. For practical purposes, effective analyte concentration can only be obtained for samples with a specific conductivity of less than 50 μS .

As in all ion exchange systems, the resin in a concentrator column has a finite capacity (i.e., the column can “strip” a given amount of ions from the sample matrix). The analytes are not quantitatively retained when the capacity of the column is exceeded.

When estimating the capacity of a concentrator column, it is important to consider that the column is used in a dynamic state (i.e., liquid is flowing). This reduces the static capacity because the ions have less opportunity to interact with the resin surface. The static capacity of a concentrator column is stated in the column manual. The dynamic capacity, which is dependent on flow rate and the analyte affinity for the resin, is approximately 50% of the total static capacity.

The situation is more complicated when ions of widely different affinities for the resin are present in the sample. An ion(s) may act as an eluent if its affinity for the ion exchange resin is greater than the affinity of the ions already associated with the resin. For example, anions such as sulfate act as eluents causing dis-

placement of more weakly retained anions such as fluoride and chloride when concentrations are close to or exceed the dynamic capacity of the concentrator column. Early breakthrough is possible when an ion(s) acts as an eluent.

Breakthrough volume, which is defined as the volume of sample that causes an ion(s) of interest to be eluted from the concentrator column, must be determined for a simulated sample matrix to ensure quantitative retention of the analytes of interest and accurate results for the analysis.

Breakthrough volume is determined as follows:

1. Prepare 1 L of the sample or a solution that closely simulates the type of sample to be analyzed. For example, if the sample contains ammonia, the simulated sample should also contain ammonia. Ammonia in solution exists as ammonium and hydroxide ions. The resulting hydroxide (OH^-) ion will act as an eluent when concentrating anions.
2. Prepare a 1 mg/L standard of the first eluting ion of interest.
3. Set up the ion chromatograph as shown in Figure 6 and flush the concentrator column with the eluent until a stable baseline is achieved.
4. Switch to the simulated sample as an eluent, obtain a stable baseline, and inject a 50 μL portion of the 1 mg/L standard.
5. Record the resulting chromatogram and calculate the breakthrough volume (4 mL/min flow rate) as shown in the Figure 7.

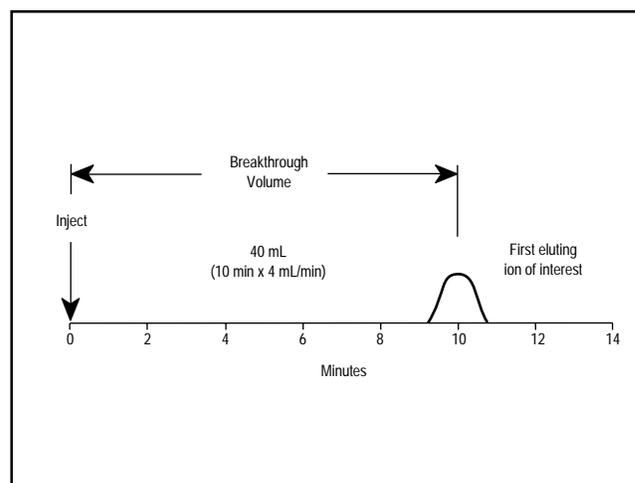


Figure 7 Breakthrough volume determination.

An alternate method for determining breakthrough volume:

1. Set up the ion chromatograph with the intended method.
2. Prepare a standard with analytes present at the highest anticipated concentration spiked in the sample or a simulated sample matrix.
3. Concentrate the standard using increasing sample volumes and the recommended concentrator column flow rate and record the chromatogram for each sample volume.
4. Plot peak area versus sample volume. Deviation from linearity indicates the breakthrough volume. In the example in Figure 8, breakthrough occurs at a sample volume of 25 mL.

For practical purposes, the amount of sample concentrated should not exceed 75% of the breakthrough volume. This will insure that there is a safety margin, particularly when a sample of slightly higher ionic concentration is analyzed.

CONCLUSION

Concentrator columns are used to concentrate analytes from large volumes of sample. Lower detection limits are achieved by concentrating from larger sample volumes. However, to obtain accurate and reproducible results, proper technique must be used to minimize contamination and to provide reproducible sample volumes. Method validation (especially determination of concentrator column breakthrough volume) is required to achieve accurate quantitative results.

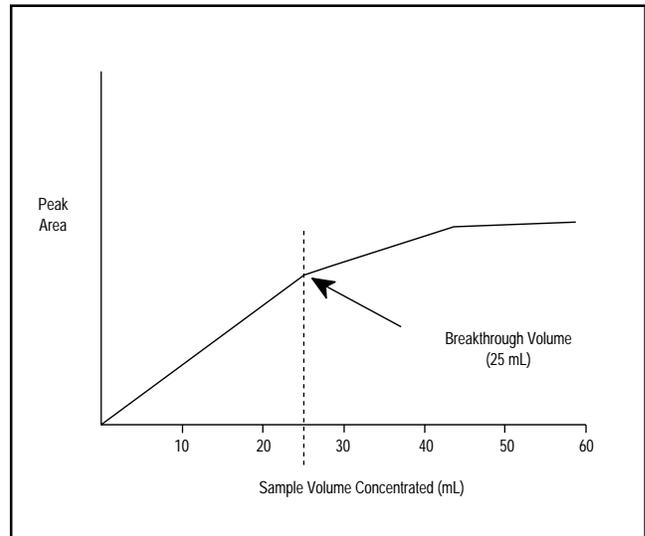


Figure 8 Breakthrough volume determination (alternate method).

APPENDIX A: DIONEX STANDARDS

Dionex standards are traceable to *NIST Standard Reference Materials* and are shipped with a "Certificate of Analysis" verifying the concentration.

Anion Standards

Combined Five Anion Standard, P/N 37157

Contains: Fluoride (20 mg/L), chloride (30 mg/L), nitrate (100 mg/L), phosphate (150 mg/L), and sulfate (150 mg/L)

Fluoride Standard (1000 mg/L), P/N 37158

Chloride Standard (1000 mg/L), P/N 37159

Sulfate Standard (1000 mg/L), P/N 37160

Cation Standard

Combined Six Cation Standard, P/N 40187

Contains: Lithium (50 mg/L), sodium (200 mg/L), ammonium (400 mg/L), potassium (200 mg/L), magnesium (200 mg/L), and calcium (1000 mg/L)

APPENDIX B: CONCENTRATOR COLUMN PUBLICATIONS

The following Dionex publications describe specific applications that use concentrator columns:

1. Dionex Application Note 85: "Determination of Trace Anions in Isopropyl Alcohol".
2. Dionex Application Note 86: "Determination of Trace Cations in Power Plant Waters Containing Morpholine".
3. Dionex Application Update 102: "Trace Anions in Power Plant High-Purity Water and Borated Water".



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