# Accurate and Precise Automated Dilution and In-line Conductivity Measurement Using the AS-AP Autosampler Prior to Analysis by Ion Chromatography

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## Key Words
Automated Dilution, IC, pH Accessory, Sample Conductivity

## Goal
Demonstrate accurate and reliable sample dilutions using the Thermo Scientific™ Dionex™ AS-AP Autosampler and outline the use of in-line conductivity measurement with the Thermo Scientific Dionex AS-AP Sample Conductivity and pH Accessory prior to analysis by ion chromatography.


## Introduction
Ion chromatography (IC) is a well-established method for determination of ionic analytes. Levels of ions can be readily quantified down to parts per trillion (ppt) using suppressed conductivity by a Thermo Scientific™ Dionex™ Reagent-Free™ IC (RFIC™) system. Low analyte concentration measurements often push the limits of detection using IC, while at the other extreme, samples such as hydraulic fracking wastewater (from oil and gas production) and brine solutions (used in electrolysis reactions), can have levels that exceed 150,000 mg/L.[1] Such high concentrations necessitate loading less sample volume or diluting prior to injection to avoid exceeding column capacity and to ensure that the concentrations determined fall within the calibration range. The latter is particularly important when regulated methods are used, which typically prescribe a concentration range for each analyte.

There are several ways to determine sample concentration and thus the need for dilution or otherwise reducing the amount of sample injected:

- Manual conductivity measurement followed by dilution – this is tedious, labor intensive, and prone to errors.
- AutoDilution using Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software – samples are run undiluted and then, based on the peak height or area of analytes in the resultant chromatogram, the amount of sample injected is reduced before re-analysis using:
  - A smaller volume by partial loop injection[2]
  - A smaller sample injection loop[3,4]
  - Dilution by autosampler[5]
- In-line conductivity measurement using the Dionex AS-AP Sample Conductivity and pH Accessory – sample conductivity is determined prior to injection and, if the conductivity measured exceeds a specified cut-off value, the sample is either automatically diluted or less of it is injected (as above).

This Technical Note (TN) will discuss automated dilutions using the Dionex AS-AP Autosampler with and without the Dionex Sample Conductivity and pH Accessory, review experimental data, and recommend conditions for obtaining optimal results.

## Equipment

- Thermo Scientific Dionex ICS-2100 Integrated RFIC system
- Dionex AS-AP Autosampler
  - Dionex AS-AP Sample Conductivity and pH Accessory (Dionex P/N 074923) with the included pH electrode port plug and seal installed
- Chromeleon Chromatography Data System version 6.8 (release 6.80 DU11c or later) or 7 (release 7.1 SR1 or later)

## Reagents and Standards

- 18 MΩ-cm resistivity degassed deionized water
- Thermo Scientific Dionex 1000 µS conductivity standard (Dionex P/N 080172)
- J.T. Baker Sodium chloride, Ultrapure (P/N 4058-05)

| **Chromatographic Conditions** | |
|---|---|
| Column: | Thermo Scientific™ Dionex™ IonPac™ AG18 column, 4 × 50 mm<br>Dionex IonPac AS18 column, 4 × 250 mm |
| Eluent Source: | Thermo Scientific Dionex EGC III KOH cartridge |
| Eluent: | 39 mM KOH |
| Flow Rate: | 1.0 mL/min |
| Column Temp. | 30 °C |
| Inj. Volume: | 25 µL |
| Detection: | Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor*, recycle mode, 97 mA |
| Background Conductance: | < 2 µS |
| Noise: | < 3 nS |
| System Backpressure: | 2050 psi |

** Equivalent or improved results can be obtained using the Thermo Scientific™ Dionex™ ERS™ 500 Electrolytically Regenerated Suppressor.*

Part numbers of the consumables used in this document are listed in Table 1. For best results the vials specified should be used.

Table 1. Consumables list.

| Product Name | Description | Dionex Part Number |
|---|---|---|
| Dionex EGC III KOH cartridge | Eluent generator cartridge | 074532 |
| Thermo Scientific Dionex CR-ATC column | Continuously regenerated anion trap column | 060477 |
| Dionex IonPac AS18 column | Separation column, 4 mm i.d. | 060549 |
| Dionex IonPac AG18 column | Guard column, 4 mm i.d. | 060551 |
| Dionex AERS 500 suppressor | Suppressor cartridge, 4 mm i.d. columns | 082540 |
| Dionex AS-AP Autosampler Vials | Polystyrene vials with caps and blue septa, 10 mL, package of 100 | 074228 |
| | Polypropylene vials with caps and blue septa, 1.5 mL, package of 100 | 079812 |

## Standard Preparation

Prepare a 20 g/L chloride stock solution by adding 2 g of sodium chloride to a volumetric flask and adding deionized water to the 100 mL mark. Prepare manual dilutions of this stock by pipetting the appropriate volumes into a volumetric flask and then adding deionized water to 100 mL. All stock solutions were stored at 4 °C and aliquots were dispensed as needed prior to use.

It is important to use 18 MΩ-cm resistivity, deionized water for eluent and autosampler flush solutions to avoid system contamination, decreased sensitivity, and poor calibration. Degassing the deionized water by vacuum filtration prior to use is also good practice.

## Instrument Setup

Install, hydrate, and condition the Dionex EGC III KOH eluent generator cartridge. This cartridge requires at least 2000 psi of backpressure for optimal operation. Install and hydrate the Dionex CR-ATC trap column and the Dionex ASRS 300 Anion Self-Regenerating Suppressor. Hydrate the devices and finish the system setup according to the product manuals and the Dionex ICS-2100 Operator's Manual.[6–9] Install and condition the columns for 30 min prior to installing the columns in-line with the suppressor. If total system backpressure is < 2000 psi, install one or more backpressure coils between the Dionex CR-ATC column and the injection valve to increase the system pressure to between 2000 and 3000 psi.

## AS-AP Autosampler Configuration and Parameters

- Syringe: 1 mL
- Buffer Line Volume: 1.2 mL
- Wash solution: 18 MΩ-cm resistivity degassed deionized water

The default parameters for wash volumes and syringe speeds were used except where indicated. Refer to the Dionex AS-AP Sample Conductivity and pH Setup and Operation Guide[10] and the Dionex AS-AP Autosampler Operators Manual[11] for recommended ranges.

## AS-AP Sample Conductivity and pH Accessory Setup

Figure 1 shows the Dionex AS-AP Sample Conductivity and pH Accessory. For this application, the pH electrode is not used to minimize the amount of sample required to determine conductivity. Install the pH Electrode Port Plug (Figure 1B) in the pH electrode position as shown in Figure 1A.

To ensure accuracy, the conductivity of the Dionex AS-AP Sample Conductivity and pH Accessory was calibrated prior to use. After setting the zero point of the accessory using deionized water a 1000 µS standard was introduced into the accessory to establish a cell calibration constant (using Chromeleon CDS) which was used for all subsequent measurements.

Figure 2 depicts the setup used when the Dionex AS-AP Sample Conductivity and pH Accessory is installed in the Autosampler. It is recommended that a service engineer install this accessory. In the analyses described in this Technical Note, installation of the pH electrode port plug reduced the sample volume required to only ~600 µL, compared to the ~2000 µL volume required with the pH probe installed. This lower volume permits the use of the standard 1 mL syringe and 1.2 mL buffer line. For further setup and pH electrode use information, refer to the Accessory Setup and Operation Guide.[10]

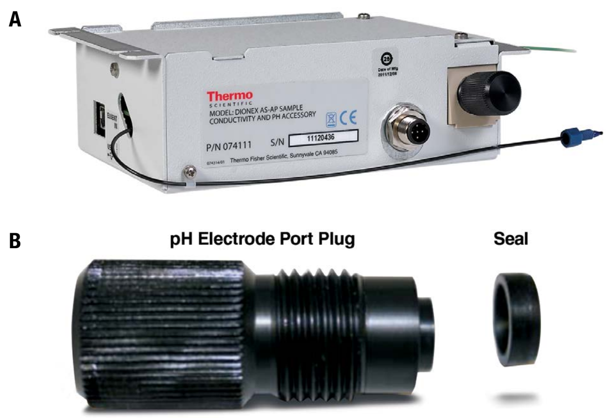


Figure 1. A) Dionex AS-AP Sample Conductivity and pH Accessory.
B) pH electrode port plug and seal.

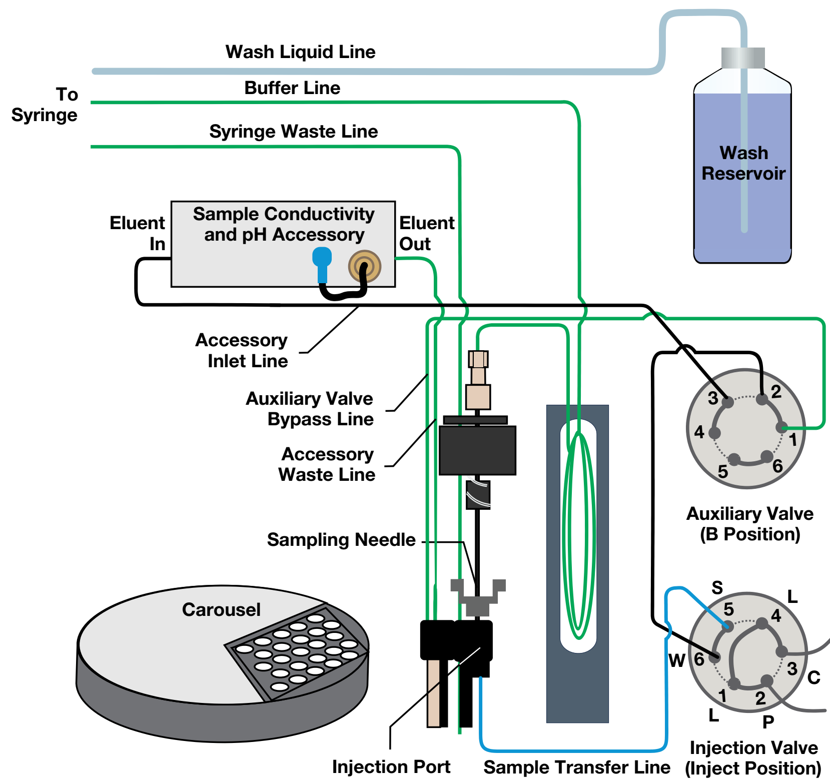


Figure 2. Dionex AS-AP Autosampler plumbing schematic for Push Mode with the Dionex AS-AP Sample Conductivity and pH Accessory.

## Chromeleon CDS Method Parameters

### Conditional Settings Using In-line Conductivity

The Chromeleon software uses a simple Program Wizard to set up the pH and Conductivity measurement parameters and their application to pre-injection decisions for sample handling. High and low limits for the sample conductivity can be specified and if the value determined lies outside of this range, the sample can be:

- Skipped
- Processed using an alternate program that specifies
  - Automated dilution
  - Smaller volume partial loop injection
  - Injection via a smaller sample loop
- Use IF-ENDIF logic to activate other commands

The use of alternate programs as described above is not yet supported in Chromeleon 7 software.

Figure 3 shows the Chromeleon 6.8 CDS Program Wizard page specifying that the in-line measurement option should be used to measure conductivity, the acceptance limits for the sample (0–1500 µS), the volume to use (600 µL), and what action to take if the value measured is outside of these limits (Process with 100-fold_dil.pgm).

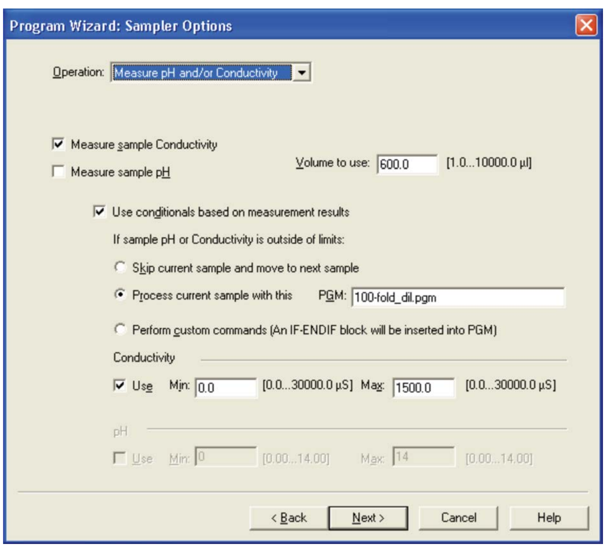


Figure 3. Chromeleon 6.8 CDS Program Wizard: Sampler options for the AS-AP Sample Conductivity and pH Accessory.

During a run, the conductivity readings are displayed on the Dionex AS-AP Conductivity/pH ePanel (Chromeleon 7.0 CDS and above) or Conductivity/pH Values Control Panel (Chromeleon 6.8). These readings can also be included in results tables by inserting a report column for "Sample Conductivity". In Chromeleon 6.8 CDS, this column can also be added to a sequence table. For more data viewing options see the Dionex AS-AP Sample Conductivity and pH Operator's Guide.[10] The audit trail will also contain the conductivity reading from each sample as exemplified by the excerpt shown in Figure 4. Also noted are the stability of the measurement, the conductivity limits (Lines 3 and 4); the conditional statement (Line 5), conditional result (Line 6), and the program that was run based on this result (Line 11).

```
{Sampler} Log Sample_Conductivity: 6477.3
{Sampler} Log Sample_ConductivityStability: Stable
MinConductivity = 0.0
MaxConductivity = 1500.0
If  Sample_Conductivity < MinConductivity OR Sample_Conductivity >
MaxConductivity: Yes
Wash
Wait  Ready
Wait finished
Delay 1.0 sec.
Branch "100-fold_dil.pgm"
Wait  Ready
```

Figure 4. Audit trail excerpt showing the conductivity reading, stability, and limits, conditional command, and the conditional program.

## Program Setup for Sample Dilution

With Chromeleon software, programs can be created to perform dilutions into a single vial or sequentially into multiple vials using the Dionex AS-AP Autosampler. Figures 5 and 6 display Program Wizard sampler options that were used to create a program for draw/dispense mixing of a 100 µL sample with 900 µL deionized water using 1.5 mL vials.

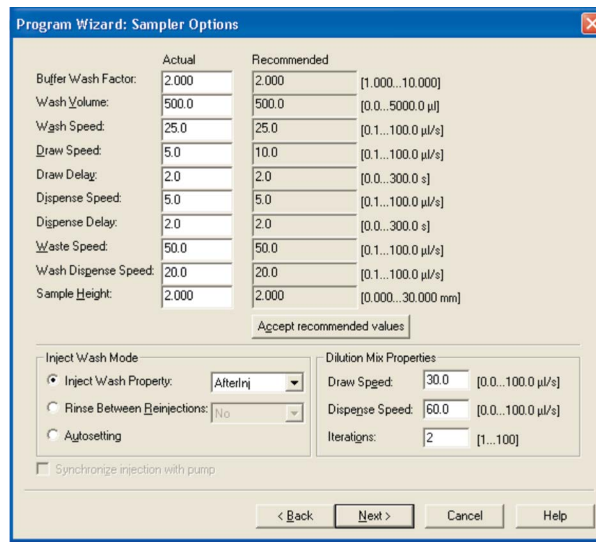


Figure 5. Chromeleon 6.8 CDS Program Method Wizard: Sampler settings for Wash Volumes and Syringe Speed.

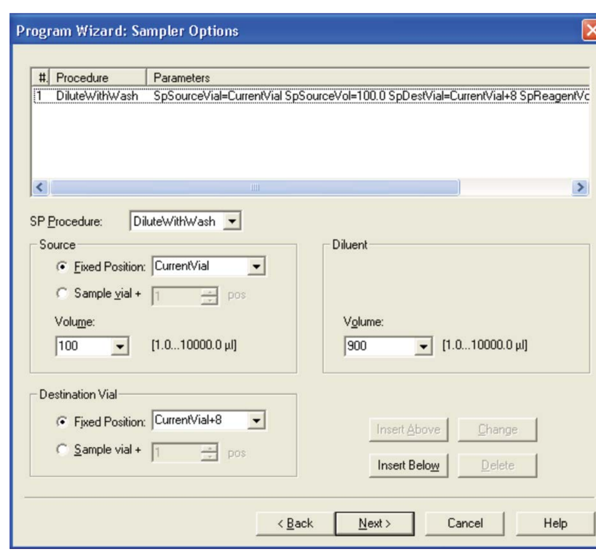


Figure 6. Chromeleon 6.8 CDS Program Method Wizard: Dilute with wash settings.

Note that in the "DiluteWithWash" step shown in Figure 6, the destination vial specified is "CurrentVial+8", which allows the 1.5 mL vial rack (40 position) to be loaded so that empty dilution vials can be positioned in the row adjacent to the one containing samples. Samples and dilution vials therefore occupy alternate rows in the rack.

## Results and Discussion

To ensure that the data generated was statistically significant, at least five replicates were used for each set of experiments. To determine the data precision, the percent relative standard deviation (%RSD) was calculated by dividing the standard deviation by the average value of the replicates and then multiplying the result by 100. Accuracy is a measure of how close the experimental values obtained are to the true values. For the dispensing data presented in Table 3, the accuracy was determined by dividing the mass of the solution dispensed by the Dionex AS-AP Autosampler by the mass expected based on the volume specified in Chromeleon software and the density of the solution dispensed. For the accuracy of data presented in Tables 4–7, the average chloride peak area from chromatograms obtained from Dionex AS-AP Autosampler dilutions was divided by that obtained from dilutions performed manually. These values were converted into a percentage by multiplying by 100. Thus, a value of 100 indicates an exact match of the experimental with the theoretical.

### Conductivity Data Reproducibility

To verify the reproducibility of the conductivity data obtained by the Dionex AS-AP Sample Conductivity and pH Accessory using the setup and conditions outlined here, measurements were obtained from five injections of either a 2 or 0.2 g/L chloride solution. Table 2 shows the average conductivity and reproducibility. As can be seen, for both concentrations the %RSD of the conductivity measurements made was <0.06. These samples were also measured manually using a portable conductivity meter (VWR Cat. No. 23226-505) and comparable values were obtained.

Table 2. Reproducibility of conductivity measured by the Dionex AS-AP Sample Conductivity and pH Accessory.

| | Conductivity (µS/cm) | |
|---|---|---|
| Chloride Concentration (g/L) | Average | %RSD |
| 2 | 6545 | 0.058 |
| 0.2 | 683.1 | 0.034 |

**Conditions**
Draw/Dispense Speed: 20/10 µL/sec
Sample Volume Drawn: 600 µL

### Dionex AS-AP Autosampler Dispensing Accuracy

When performing automated dilutions, the two variables that have the greatest impact on results are how precisely liquid is dispensed and how thoroughly these solutions are mixed. If the mechanical dispensing of liquid is not precise or if the subsequent mixing step is insufficient, the true concentration of the starting material will not be accurately determined.

To evaluate the precision and accuracy of the Dionex AS-AP Autosampler, several volumes were dispensed into vials that were weighed before and after liquid addition on an analytical balance with ± 0.001 mg precision. The difference in mass obtained was compared to the theoretical amounts expected based on the volume specified in Chromeleon software. For measurements in which 20 g/L sodium chloride was dispensed (5–70 µL), the expected mass value was adjusted to account for this solution's increased density. To facilitate data interpretation, in all of the tables presented, cells with accuracy < 95% or > 105% or %RSD > 1 are highlighted in blue, indicating unacceptable conditions. As shown in Table 3, the Dionex AS-AP Autosampler dispensed both large and small volumes with an accuracy > 98%. The lone exception was the smallest that was used, 5 µL.

Table 3. Dispensing accuracy of the Dionex AS-AP Autosampler based on mass.

| | | Mass (mg) | | | |
|---|---|---|---|---|---|
| Draw/Dispense Speed (µL/sec) | Volume | Average | %RSD | %Accuracy[A] | Time (min)[B] |
| 10/5 | 6930 | 6894.8 | 0.0127 | 99.5 | 30 |
| 50/25 | 6930 | 6898.2 | 0.0059 | 99.5 | 12 |
| 50/25 | 4995 | 4973.3 | 0.0894 | 99.6 | 9 |
| 50/25 | 4950 | 4926.8 | 0.0032 | 99.5 | 9 |
| 50/25 | 1980 | 1968.9 | 0.0747 | 99.4 | 4 |
| 50/25 | 1485 | 1470.8 | 0.108 | 99.0 | 4 |
| 10/5 | 70 | 71.2 | 0.12 | 99.8 | 3 |
| 10/5 | 50 | 50.5 | 0.38 | 99.0 | 2 |
| 10/5 | 20 | 20.1 | 0.67 | 98.4 | 2 |
| 10/5 | 15 | 15.3 | 0.86 | 100.0 | 2 |
| 10/5 | 5 | 4.7 | 3.09 | 92.7 | 2 |

A: Accuracy adjusted based on density (1.02 g/mL for 20 g/L $Cl^-$ solution, which was used for all volumes < 1 mL).
B: Approximate draw and dispense time per vial.

This volume may approach the limit of what can be accurately dispensed by the one mL syringe. The 6930 µL dispense experiments were performed at both a faster (50/25 µL/sec) and slower (10/5 µL/sec) draw/dispense speed. Since the resultant accuracy and %RSD was approximately equivalent for both of these conditions, the faster speed was used subsequently for volumes > 1 mL. As expected, slower draw and dispense speeds resulted in longer overall run times, which are a consideration if rapid sample throughput is a priority.

### Effect of Final Volume on Mixing by Automated Carousel Shake

To evaluate the effect of volume on the reproducibility and accuracy of mixing by automatically shaking the carousel, different volumes of 20 g/L chloride were dispensed into 10 mL vials containing deionized water to obtain 100-fold dilutions. The vials were then mixed by shaking the autosampler carousel 10 times at the maximum rotation speed, which is set by default. Table 4 shows that, as the final volume used for dilutions was decreased from 7 to 2 mL, the accuracy of the peak areas, following Dionex AS-AP Autosampler mixing, increased from 90 to 99% and the %RSD improved from 27 to 0.8%. This improved accuracy and reproducibility was due to the more thorough mixing that occurs when the final volume is a lower percentage of the vial capacity.

Table 4. Dionex AS-AP Autosampler 100-fold dilution of 20 g/L chloride into deionized water in 10 mL vials using shaking to mix.

| | Chloride Peak Area (µS*min) | | | |
|---|---|---|---|---|
| **Final Volume (mL)** | **Average** | **Std Dev** | **%RSD** | **%Accuracy** |
| **7** | 50.7 | 13.8 | 27.2 | 90.3 |
| **5** | 47.6 | 10.1 | 21.1 | 84.7 |
| **2** | 56.1 | 0.45 | 0.80 | 98.3 |

**Conditions**

| | | | |
|---|---|---|---|
| Dilutions: | Final Vol. | Sample Vol. | Water Vol. |
| | 7 mL | 70 µL | 6930 µL |
| | 5 | 50 | 4950 |
| | 2 | 20 | 1980 |
| Solution Addition: | Draw/Dispense Speed | | |
| | 50/25 µL/sec (water) | | |
| | 10/5 (sample) | | |

### Effect of the Order of Dispensing on Mixing

In the experiments summarized in Table 4, water was dispensed first and then sample, followed by mixing. To investigate the impact that the order of liquid dispensing has on mixing, 50 µL of 20 g/L chloride was dispensed into vials first and then 4950 µL water added (Table 5). Adding diluent to sample greatly facilitated mixing, as evidenced by the 10-fold improvement in %RSD and an increase in accuracy from 85 to 97%.

Table 5. 100-fold dilution in which water was dispensed into an aliquot of 20 g/L chloride.

| | Chloride Peak Area (µS*min) | | | |
|---|---|---|---|---|
| **Final Volume (mL)** | **Average** | **Std Dev** | **%RSD** | **%Accuracy** |
| **5** | 55.0 | 1.16 | 2.10 | 97.4 |

**Conditions**

| | | |
|---|---|---|
| Dilutions: | Sample Vol. 50 µL | Water Vol. 4950 µL |
| Solution Addition: | Draw/Dispense Speed 50/25 µL/sec (water and sample) | |

### Effect of Position on Mixing by Automated Carousel Shake

It was observed that when shaking was used to mix dilutions in 10 mL vials, there was a positional effect. That is, the %RSD and accuracy improved when the vials were positioned towards the periphery of the autosampler rack (i.e., rows C and D). The reason for this difference is that, in the outer rows, vials are subjected to greater centrifugal force during each rotation and when the carousel movement is halted, liquid is mixed more vigorously.

### Draw and Dispense Mixing in 10 mL Vials

An alternate mode of mixing known as Draw and Dispense can be used instead of mixing by carousel shake. With this method, liquid is drawn up by the needle positioned close to the bottom of the vial (2 mm from bottom) and then dispensed at a higher position (12 mm). While slower than shaking, draw and dispense mixing can be used for all vial sizes, whereas mixing by carousel shaking is not effective using small sample vials (1.5 mL) due to the constrained liquid movement resulting from the reduced vessel diameter. To evaluate the effect of draw and dispense mixing using 10 mL vials, 70 µL of 20 g/L chloride was added to 6930 µL deionized water and then mixing was performed by drawing and dispensing 1 mL of solution five or ten times. As can be seen in Table 6, the accuracy and %RSD improved from 135 to 103% and 15.8 to 6.0, respectively, when the mixing iterations were increased from five to ten.

Table 6. Draw and dispense mixing of water into 20 g/L chloride in 10 mL vials.

| | Chloride Peak Area (µS*min) | |
|---|---|---|
| **Iterations** | **5** | **10** |
| **%RSD** | 15.8 | 6.03 |
| **%Accuracy** | 135.0 | 103.0 |

**Conditions**

| | | |
|---|---|---|
| Dilution: | Sample Vol. 70 µL | Water Vol. 6930 µL |
| Solution Addition: | Draw/Dispense Speed 50/25 µL/sec (water and sample) | |
| Mixing: | Draw/Dispense Speed 50/50 µL/sec | Volume 1 mL |

### Draw and Dispense Mixing in 1.5 mL Vials

To evaluate the effectiveness of draw and dispense mixing in 1.5 mL vials (for which carousel shake mixing is not effective), solutions were dispensed for either 10- or 100-fold dilutions and 70% of the final volume was used for two mixing iterations. As can be seen in Table 7, the %RSD was less than 1% and the accuracy of the peak area was greater than 97% for both 10- and 100-fold dilutions, comparable to the values obtained when 2 mL volumes in 10 mL vials were mixed by shaking. Additional draw/dispense repetitions did not improve mixing using the conditions outlined here.

Table 7. Draw and dispense mixing of water aliquoted into 20 g/L chloride in 1.5 mL vials.

| | Chloride Peak Area (µS*min) | |
|---|---|---|
| **Dilution** | **10-fold** | **100-fold** |
| **%RSD** | 0.43 | 0.69 |
| **%Accuracy** | 99.6 | 97.4 |

**Conditions**

| | | | |
|---|---|---|---|
| Dilution: | Fold | Sample Vol. | Water Vol. |
| | 10 | 100 µL | 900 µL |
| | 100 | 12 | 1188 |
| Solution Addition: | Draw/Dispense Speed<br>5/5 µL/sec (water and sample) | | |
| Mixing: | Draw/Dispense Speed<br>30/60 µL/sec | Volume<br>70% final | Iterations<br>2 |

## Conclusion

The Dionex AS-AP Autosampler with integrated Dionex AS-AP Sample Conductivity and pH Accessory in combination with Chromeleon software automates the process of determining the need for and then performing dilution of samples containing high levels of ions. Specifying a conductivity cutoff, above which a sample will be automatically diluted, prevents the overloading of IC columns and ensures that analyte concentrations are accurately determined, saving both time and reagents.

Based on the results presented here, the following are recommendations for optimal automated sample dilutions:

- 10 mL vials
  - 100-fold dilutions: use mix by shaking with 2 mL final volume, 10 iterations, placing dilution vials in rows B and D (Figure 7).
  - 1000-fold dilutions: use mix by shaking with 5–7 mL final volume, 20 iterations, placing dilution vials in rows B and D; alternatively, use 10- and 100-fold vial to vial dilutions.
  - For dilutions > 1000-fold, use a multi-step dilution procedure. For example, a 10,000 to 1 dilution would be best done by two stepwise 100-fold dilutions.
- 1.5 mL vials
  - For 100-fold dilutions use 1.2 mL final volume with 2 draw/dispense iterations.
  - For dilutions > 100-fold, use a combination of vial to vial dilutions.

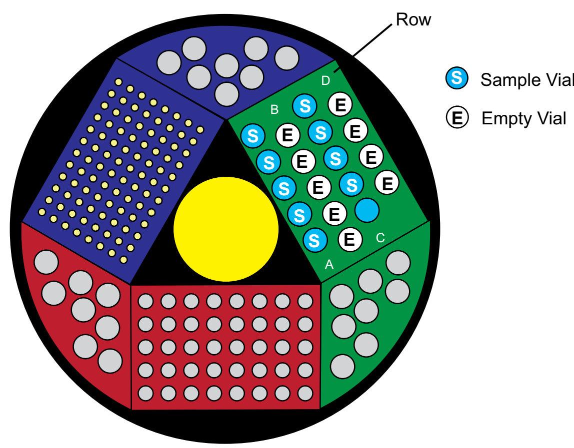


Figure 7. Suggested positioning of 10 mL vials for mixing by carousel shake in the Dionex AS-AP Autosampler tray.

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