

Automated Sample Preconcentration of Metals in Drinking Water for Inductively Coupled Argon Plasma (ICAP) Spectroscopy

INTRODUCTION

Ion exchange is a technique that has long been used for concentration and separation of trace metals. The documentation of ion exchange is extensive and its application for sample pretreatment prior to spectroscopic analysis is well known. Ion exchange offers a solution to detection limits commonly experienced when analyzing ultratrace concentration of metals in high purity water or drinking water by inductively coupled argon plasma (ICAP) spectroscopy. Using a simple form of mixed bed ion exchange resin, the analytes of interest, both anions and cations, can be concentrated from a relatively clean matrix. In this technical note, we describe a technique based on direct coupling of a sample preconcentration system (an ion chromatograph) to a simultaneous ICAP for trace metals in drinking water. This sample preconcentration method lowers the ICAP detection limits at least 50-fold for most metals.

EQUIPMENT

A sample preconcentration system comprising:
Advanced Gradient Pump (AGP, P/N 42144/115V;
P/N 42145/220V)
Sample Concentration Module (SCM, P/N 42134/115V,
P/N 42135/220V)
IC/ICAP Installation Kit (P/N 43169; contains
eluent containers, air regulator, tubing, power cords
and fittings for installation)
IonPac® CG5 (P/N 37029), 2 required
IonPac CG2 (P/N 35370), 3 required

Any Thermo Jarrell Ash (TJA) simultaneous ICAP instrument (Model 61, 61E, 1100, 9000) can be interfaced to the Dionex IC as long as the simultaneous spectrometer is used with an IBM or IBM-compatible computer with TJA ThermoSpec software. For system automation, a ThermoSpec-supported autosampler is required. A TJA type 22 or TJA 300 autosampler can be used. The autosampler should use the large sample racks (type 24) to ensure sufficient sample volume.

Questions concerning the compatibility of interfacing a particular TJA simultaneous ICAP instrument to a Dionex IC should be directed to your TJA sales or service representative.

REAGENTS

2.0 M Ultrapure Nitric Acid (1L, P/N 33442; 6 L,
P/N 33443)

Atomic Absorption Standard (1000 ppm) for each metal
of interest

ELUENTS AND STANDARD PREPARATION

Before preparing the eluent and standard, thoroughly clean the eluent containers as directed in "System Preparation", later in this technical note. Be sure that the eluent bottle caps have a white TFE seal, NOT a black rubber seal. The 2.0 M nitric acid is available in a ready-to-use form. If you wish to prepare your own solution, Optima grade reagents (Fisher Scientific), SeaStar Ultrapure Reagents (SeaStar Chemical), and Ultrex reagents (Van Waters and Rogers Scientific) can be used. For ultratrace level determination (sub-ppb), it is necessary to use ultrapure grade. Any metal impurity in the reagents will be concentrated with your sample constituting a system blank.

Eluent 1: Ultrapure Water

Eluent 2: 2.0 M Nitric Acid

If Dionex ultrapure reagent is used, no further preparation is required. Otherwise, place 200 mL of ultrapure water into a clean 1-L glass eluent container. Add 179 g (126 mL) of ultrapure nitric acid. Add water to bring the final volume to 1.0 L and mix thoroughly.

Carrier Solution: Ultrapure Water

Working standards can be prepared from 1000-ppm atomic absorption standard solutions. Since the analytes of interest are concentrated, the concentration of the high standard used should not exceed 1 ppm. It is convenient to first prepare a 10X concentrate or stock solution of the standard, and then prepare the high standard by dilution of the stock solution.

DISCUSSION OF THE METHOD

The method described in this technical note was developed to improve the ICAP detection limit of common metals present in relatively clean matrix samples (e.g. ultrapure water, drinking water). For complex matrices such as high ionic strength or high salt matrices, the chelation concentration sample pretreatment is strongly recommended (see Dionex Technical Note 28).

The column used for sample preconcentration, the IonPac CG5, which has both anion and cation exchange sites, contains a 13- μm latex agglomerated surface sulfonated polystyrene/divinylbenzene copolymer. The anion exchange latex is low crosslinked, aminated with a hydrophilic amine and has a diameter of 0.2 μm . The cation and anion exchange capacities are 30 microequivalents and 14 microequivalents per column, respectively. The resin can be used with acid or base up to 6 M without degradation.

The sample preconcentration process consists of two steps. First, the sample is passed through the column. Metal ions are concentrated in a tight band. Then, the concentrated metals are eluted off the column with 1.5 M nitric acid and the column is ready for the next run.

The sample pretreatment system allows two measurements per run. A typical ICAP time scan is shown in Figure 1. Using 10 mL sample concentration, the ICAP detection limit is lowered at least 50 fold for most metals. It is important to use reagents and water which have very low metal contamination. Any trace metals in the reagents will be concentrated as a "blank" and subsequently eluted

with the sample. Care must be taken to minimize reagent and sample contamination during preparation and handling. Reagent purity will usually dictate the detection limits.

SYSTEM CONFIGURATION AND SET-UP

Figure 2 shows a detailed pneumatic and hydraulic schematic of the sample preconcentration system. The SCM is factory-configured for chelation concentration sample pretreatment. The following set-up procedure is required for this application.

Pneumatic Connections

Locate the four colored air tubings at the rear panel of the AGP and SCM. Using the small barbed couplers (P/N 42241), couple the air tubing together by matching the color (orange-orange, yellow-yellow, green-green and blue-blue). Next, connect about 2 ft (60 cm) of air tubing (P/N 30091) to the small barbed fitting on the back of the AGP. Insert a barbed tee (P/N 30538) into the end of this fitting. One arm of the tee will go to the nitrogen or argon source (regulator) and the other arm will go to the inlet of the eluent bottle regulator (P/N 38201). Using the required length of tubing, connect the tee to the gas source and to the eluent pressure regulator. Use the 1/4-in.-to-10/32 brass reducer (P/N 30087) and the 10/32 x 1/16-in. barbed fitting (P/N 30071) to connect the air tubing to the source regulator.

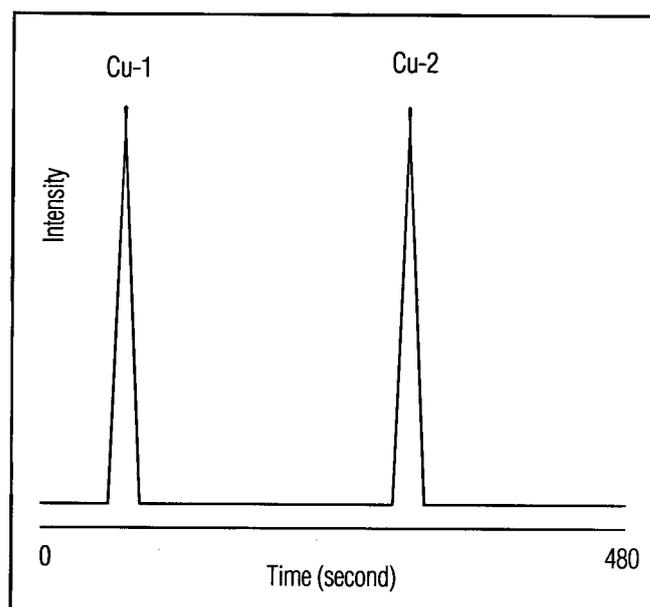


Figure 1 A typical ICAP time scan.

Next, connect the air tubing to the eluent container caps (P/N 41004). Start by cutting one of the two 1/8-in. Teflon® lines flush with the bottom of the cap. Repeat this for the other eluent container cap. Next, cut the same tubing about 2 in. (5 cm) above the eluent container cap. This line will be used to connect the argon or nitrogen for pressurizing the eluent bottles. Insert a barbed coupler (P/N 42241) into the trimmed Teflon line of cap E1. Insert a barbed tee (P/N 30538) into the trimmed Teflon line of cap E2. Connect the eluent caps using the air tubing (P/N 30091 or equivalent).

This completes the pneumatic set-up.

Hydraulic Connections

Refer to the *AGP and SCM Operator's Manuals* for details pertaining to the installation and operation of the respective modules. Begin the hydraulic connections by connecting the two eluent lines from the three eluent container caps to the front panel eluent ports of the AGP. Ensure that the eluent lines are connected to the appropriate eluent port of the AGP.

Locate the four valves in the SCM. Remove all the tubings connected to the four valves. The first valve on the far left will not be used for this configuration. Designate each valve by starting from the second valve to your right as A, B, and C. Confirm that valves A and B are controlled by E5 and valve C is controlled by E6 of the AGP. Plumb the system as indicated in Figure 2. The 0.020-in. I.D.

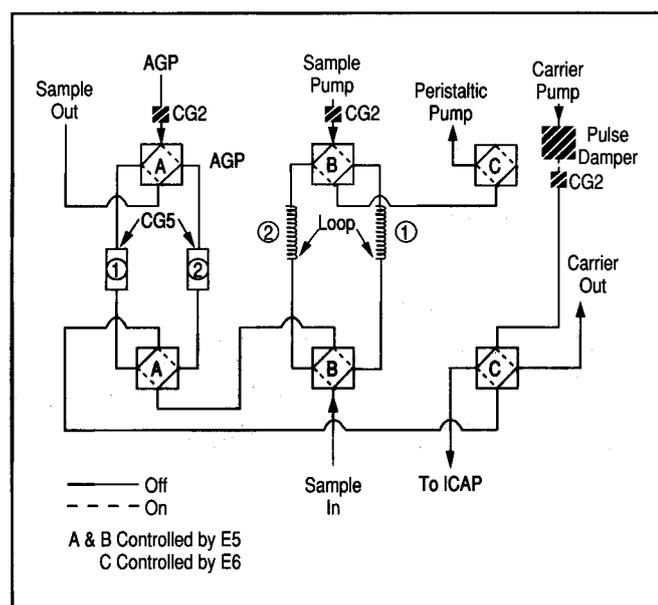


Figure 2 Pneumatic and hydraulic schematic of the sample preconcentration system

tubings (blue tubings) are used for all connections except for the sample loop. The two 10-mL sample loops can be made from 1/8-in. I.D. tubing.

Next, connect the eluent line from the 4-liter plastic eluent container (P/N 39164) to the CARRIER IN port of the SCM rear panel. Next, connect the three blue waste lines (P/N 39441) to the ports of the SCM rear panel labeled CARRIER OUT, AGP OUT, and SAMPLE OUT and place them in a waste container. For the sample inlet line, connect the 0.037-in. I.D. x 36-in. (92 cm) length of pink tubing to valve B, port 7, in the SCM. Locate the SAMPLE IN port of the rear panel and use the 1/8-in. I.D. tubing to connect this port to the peristaltic pump inlet. Finally, remove the end fitting from the 0.020-in. I.D. x 36-in. (92 cm) tubing connected to valve C, port 8, of the SCM. Using a pair of pliers, stretch the end of this tubing to taper the tubing to about two-thirds of its original outside diameter. Using about 3/8-in. (1 cm) of 0.03-in. I.D. Tygon tubing as a coupler, connect the tapered tubing to 6-in. (15 cm) of the nebulizer tubing. This is the actual liquid interface between the IC and the ICAP. Place the tubing in a waste container for the system test.

This completes the hydraulic connections.

Electrical Connections

Verify that the front PUMP 1 and PUMP 2 Power switches of the SCM are off. Using the power cords provided (P/N 96078), connect the ac receptacles on the rear panels of the SCM and AGP to the white outlets of the power strip located on the rear upper section of the system enclosure. Next, connect the ac receptacle of the power strip enclosure to an ac (110V) power outlet.

Next, install the interface cable (P/N 43044). One end of the interface cable connects to the rear panel of the AGP and the other end connects to a connector in the ICAP main power board. Start by turning off the line voltage to the ICAP intelligent controller. The circuit breaker to be turned off is located on the rear power panel of the ICAP instrument. Next, loosen (or remove) the screws on the rear power panel and carefully open the power panel to reveal the electronics. On the left side of the electronics panel is a printed circuit board containing three 12-pin Molex nylon connects in a row. Carefully remove the center Molex connector (J3-N) by gripping the sides of the connector and pulling straight up. Note the positions of the wires in the connector. Using the Molex pin extractor tool, remove the wire(s) at the 1 and 10 or 4 and 7 positions

from the Molex connector attached to the ICAP and insert them into the same positions in the Molex connector which is attached to the interface cable. Finally, plug the interface cable Molex connector into the circuit board where the original Molex connector was located. Carefully close the power panel, being careful not to pinch or sever the interface cable.

To the right of the Molex connectors are nine relay sockets. Check to see that there is a relay (labeled SOURCE or K1) installed in the relay socket. This is the relay which will be used to control the IC.

Finally, connect the interface cable to the relay connector on the rear panel of the AGP. Check to see that the AGP relay “dip” switches located on the right top cover of the AGP are in the “off” (forward) position. When the ICAP initiates an “exposure,” the AGP will be reset and will begin to execute the AGP program.

This completes the electrical connections.

SYSTEM PREPARATION

1. Confirm that the SCM is configured as shown in Figure 2. Be sure that the three IonPac CG2 columns are installed between: 1) the sample pump and valve B; 2) the carrier pump and valve C; and 3) the AGP and valve A (see Figure 2). Install the two IonPac CG5 columns in valve A.
2. Prepare 1 L of 0.2 M oxalic acid by dissolving 25.2 g of reagent grade oxalic acid dihydrate in 1 L of deionized water. This eluent will be used to clean the AGP eluent flow path.
3. Connect the 0.2 M oxalic acid to port 1 (E1) of the AGP. Pump the oxalic acid through the AGP and to waste at 2.0 mL/min for 10 minutes. Repeat this procedure for port 2. This helps to remove any trace metals from the AGP flow path.
4. Place the sample inlet tubing into the 0.20 M oxalic acid solution. Fill each of the two 1-L eluent glass bottles and the 4-L carrier bottle with 500 mL of 0.2 M oxalic acid. Enter the program listed in Table 1 on the front panel of the AGP. Refer to the *AGP Operator's Manual* for instructions on programming the AGP.
5. Before turning the pump switch on, confirm that the sample pump and carrier pump are primed. Adjust the sample pump and carrier pump flow rates at 5.0 mL/min and 2.0 mL/min, respectively. Turn the peristaltic pump switch on and adjust its flow rate to at least 5.0 mL/min. Start the AGP and run the program two or three times.
6. Replace the 0.2 M oxalic acid in the 4-L carrier bottle with water. Rinse several times. Be sure that the cap has an O-ring for proper sealing.
7. Clean two 1-L glass eluent bottles by filling them with 0.2 M oxalic acid. Allow the acid to remain in the eluent bottles for at least 4 hours. Prepare eluents as indicated in Eluent Preparation. Use caution in preparing and transferring these reagents in order to minimize contamination. Connect the filled eluent bottles to the appropriate eluent cap connected to the AGP. Be sure that the eluents are plumbed to the proper ports of the AGP (E1: water and E2: 2.0 M nitric acid). Adjust the eluent bottle regulator to 4 to 6 psi (30 to 40 kPa) and check for gas leaks.
8. Prime the AGP with each eluent as indicated in the *AGP Operator's Manual*. Be sure to tighten the needle valve upon completing the priming.

This completes the system preparation.

Table 1 Gradient Program

Time	E1	E2	E5	E6	Flow (mL/min)
0.0	25	75	0	1	1.7
4.0	25	75	1	1	1.7
9.0	25	75	0	0	1.7
E1: water E2: 2.0 M nitric acid					

System Test

The purpose of this system test is to ensure that all chromatographic and chemical components of the system are operating properly. Refer to Figure 2 for the system schematic. Be sure to check all fittings for leaks during the system test.

1. The system test begins with a test of the hydraulic system. If the system fails the hydraulic test at any point, determine the source of the plumbing error. Begin by using the program listed in Table 1 with the AGP in the stop-hold position. Press RESET to set the program to time 0.0.
2. Press start on the AGP, and the nitric acid eluent should begin to flow to the IonPac CG5-column 1 and out to the nebulizer. Check the interface tubing on valve C, port 8, of the SCM to confirm that eluent is flowing to the ICAP.
3. Next, prime the carrier pump by loosening the tubing fitting screwed into the outlet check valve. Because the carrier reservoir is pressurized (5 psi/35 kPa), the carrier solution should begin to flow out of the check valve. As the carrier solution begins to flow, turn on the carrier pump by pressing the PUMP 1 power switch located on the SCM front panel. After 5 seconds, tighten the outlet check valve tubing fitting. It is generally only necessary to finger-tighten the fitting. If the fitting leaks, tighten it another 1/8 turn using a 5/16-in. open-end wrench.
4. Set the carrier pump flow rate to about 8.00. (Refer to the *SCM Operator's Manual* for details on adjusting the flow rate.) Confirm that the carrier is flowing out of the CARRIER OUT tubing. Calibrate the carrier pump flow rate by mass or volume to 1.8 to 2.0 mL/min. Turn off the carrier pump (PUMP 1).
5. Repeat step 3 on the sample pump. Press the pump 2 power switch on the SCM front panel. Confirm that the carrier is flowing out of the SAMPLE OUT tubing. This may take a few minutes if the 10-mL sample loop is not filled. Calibrate the sample pump flow rate by mass or volume to 3.0 mL/min. Turn off the sample pump.
6. Place the sample inlet tube in a container of deionized water and start the peristaltic pump. If the sample loop is not filled, it may take about 2 minutes before DI water begins to exit the peristaltic pump tubing. Adjust the peristaltic pump flow rate to 5.0 mL/min.
7. List the AGP program to 4.0 minutes and press RUN. This will forward the program to 4.0 minutes. Check to see that the nitric acid eluent is flowing out of the ICAP interface tubing. Start the sample pump (PUMP 2) and confirm that the carrier is flowing out of the SAMPLE OUT tubing. Turn off the AGP and the sample pump.
8. List the program to 8.0 minutes and press run. Press the pump 2 power switch. Check to confirm that the carrier is flowing to the ICAP interface tubing.

This completes the system test.

SEQUENCING OF THE IC AND ICAP FOR AUTOMATION

This section describes the sequencing and operation of the system components. The IC/ICAP system has been designed to be used either manually or in the fully automated mode. Because the IC is controlled by the ICAP computer, the discussion below places the IC functions relative to the ICAP.

The system is designed to run in a fully automated mode when analyzing a series of samples. The first IC cycle performs the sample concentration process. The analytical data are not obtained until the next cycle is initiated. In other words, the result of the analysis is produced at run ($n + 1$), where n is the number of cycles or sample number.

The following describes the various operations of the IC during the gradient program:

In the first cycle ($n = 1$), the autosampler position is at sample number 1 and the result of this sample will be obtained in run ($n + 1$) or run # 2.

1.1. Time 0.0

Valves A and B switch OFF and valve C switch is ON. The peristaltic pump begins pulling sample #1 from the autosampler through loop 1 and out to waste. The AGP pumps nitric acid to the IonPac CG5-column 1 and out to the ICAP. The sample pump begins to flush the sample from loop 2 to the IonPac CG5-column 2.

2.1. Time 4.0

Valves A, B, and C switch ON. The sample pump begins to flush the sample from loop 1 to the IonPac CG5-column 1. The AGP pumps nitric acid to the IonPac CG5-column 2 and out to the ICAP. The peristaltic pump begins pulling sample #1 from the autosampler through loop 2 and out to waste.

The second cycle is initiated at time 8.0 minutes.

In the second cycle, the autosampler position is at sample number 2. The first sample has been concentrated in the IonPac CG5 column. The result of the second sample will be obtained in run #3.

2.1. Time 0.0

Valves A and B switch OFF and valve C switch is ON. The peristaltic pump begins pulling sample #2 from the autosampler through loop 1 and out to waste. The concentrated metals of sample #1 from the IonPac CG5-column 1 are eluted to the ICAP with nitric acid delivered by the AGP. The sample pump begins to flush sample #1 from loop 2 to the IonPac CG5-column 2.

2.2. Time 4.0

Valves A, B, and C switch ON. The sample pump begins to flush the sample #2 from loop 1 to the IonPac CG5-column 1. The concentrated metals of sample #1 from the IonPac CG5-column 2 are eluted to the ICAP with nitric acid delivered by the AGP. The peristaltic pump begins pulling sample #2 from the autosampler through loop 2 and out to waste.

Remember to include the blank sample (water) at the end of the analysis since the last sample requires an additional cycle to complete the analysis. In the automated mode, the gradient program is reset by the ICAP control at 8.0 minutes and never reaches the last step, time 9.0 minutes, of the gradient program. However, in the last run when the gradient is not reset, the AGP continues to run to 9.0 minutes where the IC is put in "standby" mode. If the system operates in manual mode, make sure that the new exposure starts at time 8.0 minutes.

The IC is controlled by a relay from the ICAP system controller. When an ICAP run is initiated, the computer sends a signal to the intelligent controller. The controller

either begins in a flush mode or in an exposure mode. At the initiation of an exposure, a signal is sent to the AGP. If the AGP is in the "start" mode, the signal from the ICAP controller to the AGP will reset the AGP program to time 0.0 and the program will begin to run.

IC/ICAP OPERATION

This section describes the integrated operation of the IC/ICAP system. For details on ThermoSpec software, refer to the appropriate TJA manual.

Methods Development

1. Begin by writing a ThermoSpec method titled "IC/ICAP". Under Methods Development, Set-up, select the elements of interest (F1) and also select the duplicate (F3) function for each element. Select the elements and the duplicate of each element in the order in which you want them printed in the report. Add an additional element, such as Na, which can be duplicated using the F3 function key. This element (assigned as Na-3) will be used to extend the gradient program to 8.0 minutes in the automated mode (see step 3 below for more details). Press F9 to save the element selection.

Note: The order in which the elements are printed in the analysis report can be selected under Options, F8, from the Main Menu under Methods Development.

2. Next, press F3, Output. Change the number of repeats to 1 and the concentration to ppm or ppb. Select print limits as desired. Press F9 to save.
3. For F5, Element Info, the element heading will be changed and the standard(s) concentrations entered. Start by changing the element heading. For the elements in timing group 1 (first measurement), enter the element symbol followed by "-1." For example, "Cu-1," "Fe-1," "Na-1", etc. For the elements in the timing group 2 (second measurement), enter the element symbol followed by "-2." Assign Na-3 in timing group 3.

Enter the appropriate concentration for each element. Generally, a two-point calibration routine is used, a blank "BLANK" and a high standard "HIGH STD." Be sure that the correct concentration is entered for each element and that only a high standard and a blank appear in the method. Press F9 to save. Be sure to save the entire method.

4. At this point, it is necessary to run a time scan. Press F6 for Scan and F7 for Time Scan. Remember that the time scan will be obtained in the second cycle after the sample is introduced into the IC. The Time Scan feature will be used to determine the retention times of the first and second bands. Place the sample inlet tube into the high standard and turn on the peristaltic pump when initiating the first run cycle.
5. In the Time Scan mode, the spectrophotometer monitors the plasma for a user-specified time (much like a chromatographic detector). Enter an integration "slice" of 4.8 and press ENTER. Enter 100 for the number of time slice. This will result in a time scan of 480 s. After the first cycle, press F1, run at time 8.0 minutes. The controller will go to an exposure mode (The "EXP" LED will light), and a signal sent to the AGP resets the program to time 0 and starts the AGP program. The exposure will end in 480 seconds.
7. The results of the time scan displayed on the screen should look like Figure 1. For concentrated elements, two discrete regions are present in the time scan. The first region is the first concentration band. This represents the concentrated sample from the IonPac CG5-column 1. The second region represents the second band and is subsequently eluted off the IonPac CG5-column 2. Press F1, Expand, and move the cursor to determine the time at which the peak begins to elute. Note this time for comparison to the next run. Determine the width of the peak at the base using the cursor. Typical base width is 20 to 30 seconds.

8. Press F5, Overlay, to overlay several time scans. Notice that all the concentrated metals elute with nearly the same retention times.

The time scan can be stored if required.

9. Repeat the time scan. The retention time of the peak should not vary by more than 3 seconds. Continue repeating the time scan until the retention time is ± 3 seconds. Return to the Main Menu for methods development.
10. Press F2, Internal Standards, to enter the timing groups. For timing group 1, enter a preintegration time (in seconds), determined from the first concentration band of the time scan. This preintegration time is the time from the beginning of the exposure to when a peak begins to elute. To allow for minor shifts in retention times, it is advisable to enter a preintegration time about 1 to 2 seconds less than the measured times. For the integration time, add about 5 seconds to the measured base width and enter this value (typically 30 to 40 seconds).

For timing group 2, enter a preintegration time and an integration time for the second concentration region. Calculate the values the same as you did for the first concentration region.

Since an 8-minute cycle is required for each run, a "dummy" timing group 3 is used to keep the program running until 8.0 minutes. Otherwise the exposure will end at the second preintegration time (timing group 2) and the next cycle will be initiated. For timing group 3, enter a preintegration time of 475 seconds for 5 seconds.

Press F9, Save, to complete the methods development. Be sure to save the entire method.

The system is ready for standardization. Standardization of the ICAP system with the IC is performed in the same manner as normal ICAP standardization. Standardization can be performed manually or with the autosampler.

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Dionex Corporation 1228 Titan Way P.O. Box 3603 Sunnyvale, CA 94088-3603 (408) 737-0700	Dionex Corporation Salt Lake City Technical Ctr 1515 W. 2200 South, Ste. A Salt Lake City, UT 84119-1484 (801) 972-9292	Dionex U.S. Regional Offices Sunnyvale, CA (408) 737-8522 Westmont, IL (708) 789-3660 Houston, TX (713) 847-5652 Smyrna, GA (404) 432-8100 Marlton, NJ (609) 596-0600	Dionex Canada Ltd. Mississauga, Ontario Canada (416) 855-2551	Dionex (UK) Ltd. Camberley, Surrey United Kingdom (0276) 691722	Dionex GmbH Idstein Germany (06126) 991-0	Dionex S.r.l. Rome Italy (06) 30895454	Dionex S.A. Jouy en Josas France (1) 39 46 08 40	Dionex B.V. Breda The Netherlands (076) 714800	Nippon Dionex K.K. Yodogawa-ku, Osaka Japan (06) 885-1213
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