Appendix 1. Dual-Stage Ion-Exchange Collector Column Construction, Extraction, and Analysis

General

Ion-exchange collectors (IECs) are used to determine loads of ammonium (NH_4^+) and other cations, and chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) anions from wet and dry deposition during extended periods (as much as 6 months) in a field setting. This document describes the construction of dual-stage ion-exchange columns, the extraction of cations and anions, and the analysis of NH_4^+ by ion electrode and anions by ion chromatography. Cation extracts may also be analyzed for metals and base cations by inductively coupled plasma mass spectrometry (ICP–MS). The construction of dual-stage ion-exchange columns was adapted from the single, mixed-resin bed column method described in Fenn and Poth (2004) and Fenn (2013), but this two-stage IEC allows for lower concentrations of NH_4^+ to be determined. Also described is an alternate batch extraction technique of the cation column using 200 milliliters (mL) (4x50 mL) of a 1 molar (M) solution of potassium chloride (KCl) followed by 200 mL (4x50 mL) of a 3.2 M solution of nitric acid (HNO_3) to recover NH_4^+ and cationic metals.

Construction of Dual Ion Exchange Columns

1. Before construction, all polyvinyl chloride (PVC) and polypropylene components must be rinsed and then soaked in ultrapure (U–P; 18.2 megaohm centimeters) deionized (DI) water for a minimum of 24 hours. Each male threaded component must be wrapped in Teflon tape for a secure and watertight seal. All labware that will potentially contact any inside component of the column should be polypropylene or polyethylene that has been soaked in U–P DI water.

2. *Assembling anion column.*—Refer to figure 1–1 and table 1–1 for the full component list. Note that the circumference of components E and C have been rounded off with a grinding wheel (and soaked overnight in U–P DI water) so that the fully assembled column and funnel will fit inside the 1.25-inch inner diameter, white PVC mounting tube (figs. 1–2*A* and 1–2*B*). Beginning with component C and a piece of precut polypropylene mesh spacer, roll the spacer tightly to fit inside the center of component C. Attach component B to one end of C and a pipe, component D, to the opposite end. Using a clean glass rod, pack a piece of polyfil plug into the bottom of component D. Briefly rinse the inside of the connected pieces in U–P DI water and affix to a ringstand, column side up with a waste container underneath.

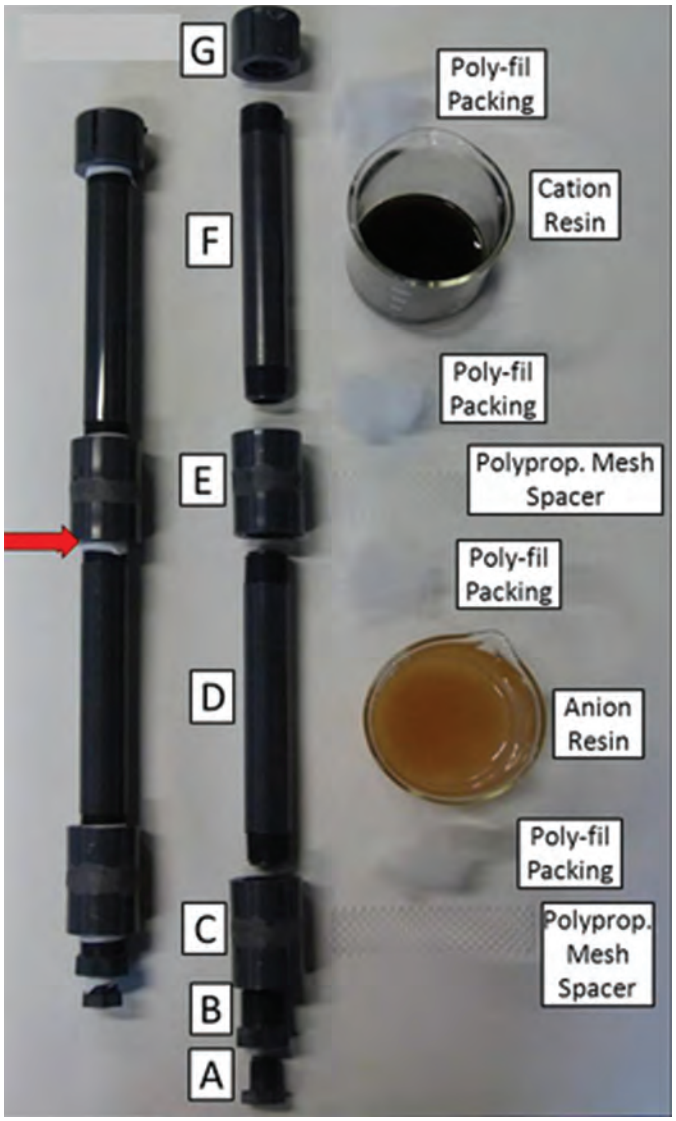

Fig. 1–1. Dual-stage ion-exchange collector components. Red arrow indicates place where sections are separated for extraction of cations or anions. Polypropylene mesh spacers are shown before they are rolled into cylindrical shape.

3. *Adding anion resin (DOWEX™ 550A UPW).*—Each resin must be thoroughly rinsed with U–P DI water (5–6 times) in a beaker. The beaker must have plenty of headspace to allow vigorous swirling of the resin. Once the anion resin has settled from the final rinse, pour off most of the excess water. Swirl again and pour 20 mL of resin into a graduated cylinder. Ensure the resin has settled completely before reading the measurement. Temporarily attach a 1-inch coupling with ½-inch reducing bushing to the top of the column to serve as filling reservoir. Carefully pour the anion resin slurry into the reservoir, being careful not to overflow. This will take several additions and U–P DI water may need to be added to the graduated cylinder to transfer all the resin. Add additional U–P DI water while gently tapping on

Fig. 1–2. An ion-exchange collector assembly. *A*, inserting the ion-exchange collector in the mounting stand. Note smoothed edges of both gray polyvinyl chloride couplings, which allow enough clearance for column to fit inside 1.25-inch diameter white polyvinyl chloride pipe pipe that is clamped inside of the mounting post legs. *B*, mounting stand containing a blank resin tube (capped and plugged) and the sample ion-exchange collector with a funnel attached. Note in this instance that protective nylon netting has not yet been placed over the funnel.

the sides and top of the column to pack the resin down. There should be at least 1 centimeter (cm) of void space at the top. Remove the filling reservoir and pack in a small amount of polyfil using a clean, glass rod. Note that the amount of polyfil used for the top of each column section should be kept to a minimum so as to avoid excessive resistance to flow.

4. *Assembling cation column.*—Tightly roll another polypropylene mesh spacer and press into the center of component E and then connect component F. Press a polyfil plug down into the bottom end. Rinse with a small amount of U–P DI water and attach the open end of E to the top of the prepared anion column.

5. *Adding cation resin.*—Follow the procedure in step 3 but using cation resin (DOWEX™ 650C UPW) and only 17 mL to fill each column. Press a small amount of polyfil into the top of the column, as in step 3. To ensure the surface tension is broken and the polyfil is fully wetted, squirt a few drops on the top of the polyfil fibers and poke with a glass rod. Let drain for about 5 minutes and then cap with components G on top and A on the bottom. Store the column upright.

6. *Funnel preparation.*—New funnels are threaded and glued onto a 1-inch coupler adaptor using the special adhesive (Weld-On 600) as described by Fenn (2013). Allow at least 2 days for the adhesive to dry. Afterwards a bead of silicone is applied to seal around the outside of the connection. To prepare funnels for field use, insert a polypropylene mesh spacer into the neck, press a small plug of polyfil onto that, and press a circular section of polypropylene mesh into the funnel opening. The completed funnel assembly is shown in figures 1–3*A* and 1–3*B* from two angles. Soon before transport, funnel assemblies are rinsed in U–P DI water and soaked overnight in round tub filled with U–P DI water. Allow the

Table 1–1. List of supplies to construct ion-exchange collectors (costs reflect 2010 prices).

[U–P, ultrapure; L, liter; kg, kilogram; ACS, American Chemical Society; cs, case; mL, millimeter; LDPE, low-density polyethylene; IEC, ion-exchange collector; PVC, polyvinyl choride; --, not applicable; aka, also known as; id, inside diameter]

Component	Merchant name and phone	Item number	Quantity	Item description	Approximate price (dollar)	Remarks
Reagents	Octochem Inc. 618–283–9360; http://dwps.octochemstore.com	Dowex 650C U–P water	1 L	DOWEX MONOSPHERE 650C U–P water cation exchange resin	115	Enough for 30 plus columns.
				Preparation		
	Octochem Inc. 618–283–9360; http://dwps.octochemstore.com	Dowex 550A U–P water	1 L	DOWEX MONOSPHERE 550A U–P water anion exchange resin	115	Enough for 30 plus columns.
				Extraction		
	Alfa Aesar Chemicals 800–343–0660	36494	1 kg	Potassium chloride ACS 99 percent minimum	150	Makes 6 L total (to extract 30 cation columns).
	Alfa Aesar Chemicals 800–343–0660	11601	1 kg	Potassium iodide, ACS 99 percent minimum	300	Makes 6 L total (to extract 30 anion columns).
	Fisher Scientific 800–766–7000	05–719–177	5x 12/cs	Precleaned 120-mL bottle, amber glass	125	For 30 cation extractions (2 bottles per sample).
	Fisher Scientific 800–766–7000	02–924–6D	3x 12/cs	250-mL LDPE bottle	125	For 30 anion extractions; pre-rinse and fill with U–P water before use.
			Containers and reagent cost for 30 IECs		**930**	
Column	McMaster–Carr 630–833–0300	4596K42	2	PVC cap 1/2 inch	5	Components listed from top to bottom as needed to make one 2-stage column; all PVC components are “schedule 80” (thick-walled, light gray).
	McMaster–Carr 630–833–0300	4882K64	2	PVC pipe nipple 1/2 x 6 inch long	8	--
	McMaster–Carr 630–833–0300	4596K52	2	PVC coupling 1/2 inch	7	--
	McMaster–Carr 630–833–0300	4596K402	1	PVC reducer bushing 1/2 x 1/4 inch	3	--
	McMaster–Carr 630–833–0300	4596K71	1	1/4 inch hex head PVC plug	2	--
	McMaster–Carr 630–833–0300	47205K24	1	PVC stopcock valve 1/4 inch	25	--
	Lowe’s or Home Depot		1 roll	Teflon pipe thread tape (large roll)	10	Use on all threaded fittings.
	Any department store		Bag	“Polyfill” pillow stuffing	5	--
	Industrial Netting 800–328–8456	XN-0260	50-foot roll	Polypropylene mesh netting (medium)	125	(Minimum order) enough for greater than 100 spacers.
			Composite cost for 30 IECs		**1,640**	--

Table 1–1. List of supplies to construct ion-exchange collectors (costs reflect 2010 prices).—Continued

[U–P, ultrapure; L, liter; kg, kilogram; ACS, American Chemical Society; cs, case; mL, millimeter; LDPE, low-density polyethylene; IEC, ion-exchange collector; PVC, polyvinyl choride; --, not applicable; aka, also known as; id, inside diameter]

Component	Merchant name and phone	Item number	Quantity	Item description	Approximate price (dollar)	Remarks
Funnel and adapter	Grainger Corp 877–423–7087	Wirthco# 90092	1	Wirthco X–large polyeth funnel (black)	20	Special order (10 minimum), distributed by Gizmos & Gadgets (aka Wirthco) 952–942–9022.
	McMaster–Carr 630–833–0300	4596K54	1	PVC coupling 1 inch,	4	To be glued to funnel.
	McMaster–Carr 630–833–0300	4596K416	1	PVC reducer bushing 1 x 1/2 inch	4	Funnel to column adapter.
	Lowe's or Home Depot		1	Sealant	6	Seal around outside of funnel–bushing.
	Grainger Corp 877–423–7087	Special order		Weld–On 600 adhesive	8	For bonding 2 types of plastic (funnel tube to 1 inch id bushing).
	Industrial nNetting 800–328–8456	XN–4510	Roll	Polypropylene mesh netting (coarse)	80	Cut into circles for screen inside bottom of funnel; (minimum order for 100+).
	Multiple distributors	#1091	Package of 144	Nylon hairnet, white, large size	10	Place over funnel in field.
			Composite cost for 30 IECs		**974**	
Mounting stand	Lowe's or Home Depot		4	"Yard–Gard" 6–foot, economy fence post	20	Economy posts are easily bendable
	Lowe's or Home Depot		1	1.25 id x 15 inches	2	Insert and clamp inside 4 mounting posts.
	Lowe's or Home Depot		3	Stainless steel hose clamp 2–3 inch diameter	5	--
	Lowe's or Home Depot		2	Stainless steel hose clamp 3–4 inch diameter	5	--
				Component cost for 30 IECs:	960	--
			Total cost for materials for 30 IECs		**4,504**	--

funnel assemblies to air dry by placing upside down on a clean bench covered with adsorbent paper and then store in a large plastic bag.

Field Deployment

1. Remove top cap and bottom plug and place in a clean zip-seal bag. Attach funnel component and insert assembly inside the white PVC tube in the mounting stand (fig. 1–2*A*), making sure not to obstruct the column's ability to drain. Attach a new nylon hair net around the funnel.
2. To retrieve, remove the funnel assembly, replace the cap in top and plug in bottom, and place in a large plastic bag along with replicates from same location. Store and ship the columns upright in a "low-boy" style cooler. Upon receipt at the laboratory, store upright in a refrigerator for up to several months before extraction.

Column Separation and Extraction

1. To rinse the column, remove the top cap and upper polyfil plug from the upper (cation) column. Remove any visible dirt or debris from around the inside of the top part of the column using one or more cotton swabs

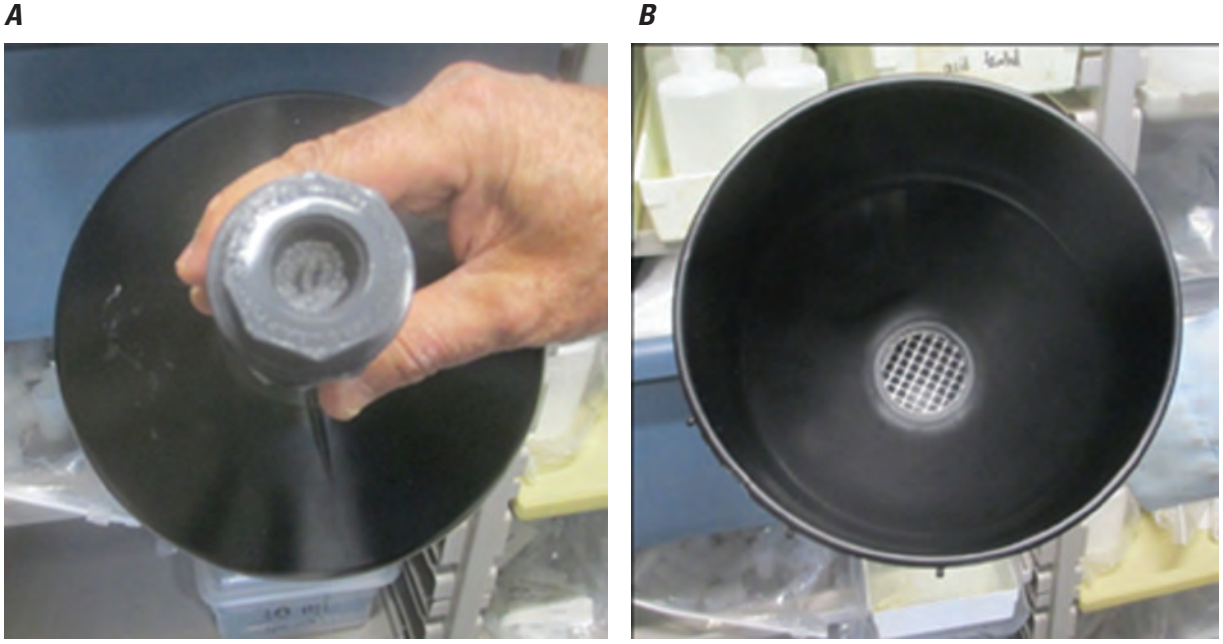

Fig. 1–3. An ion-exchange collector funnel assembly. *A*, bottom view of the funnel assembly showing the rolled section of polypropylene mesh inserted into threaded 1-inch to ½-inch reducing adaptor. *B*, top view of the funnel showing the circular section of polypropylene mesh pressed into the opening. Below that is the small mat of polyfil that was pressed into the upper part of funnel stem.

rinsed with U–P DI water. Remove the bottom plug and attach a ½- to 1-inch adaptor with 1-inch PVC coupling component to the top to serve as a filling reservoir. Rinse the 2-stage column with 50–100 mL U–P DI water and tap on the sides of the coupling between the upper and lower columns to encourage any resin that may have migrated into the coupling during shipment to settle back downward. Allow the column to drain completely (about 5 minutes) and then, using a clean gloved hand, push downward on the reservoir while making an airtight seal to plunge out any residual water.

2. Separate the two stages at the joint connecting the cation column and the anion column (red arrow on fig. 1–1). Cap the lower column, replace the bottom plug, and store upright. Extract the upper column in column mode or batch mode as described below.

3. To prepare solution for cation extraction, prepare a 1 M solution of KCl as the eluent; for the anions, prepare a 1 M solution of potassium iodide (KI) (each as American Chemical Society grade, 99+ percent). The KCl solution is made slightly acidic by adding 1 mL of a 3.2 M solution of HNO_3 per 500 mL (to stabilize as NH_4^+). Eluents should be made fresh daily; each column requires 200 mL. If metals are to be measured, the cation column is extracted secondly with 200 mL of a 3.2 M solution of HNO_3 after the KCl treatment because some metals are bound more strongly than NH_4^+, and HNO_3 is a more favorable matrix for analysis of the metals by ICP–MS. Generally, the batch method is preferred if metals and NH_4^+ will be measured.

Cation Extraction (Column Mode)

1. Attach a clean filling reservoir to the top of the column and affix a stopcock to the bottom of the column. Securely clamp the column to a ringstand. Extracts can be collected in a single 250-mL bottle or in two 125-mL bottles. For NH_4^+, a total of 200 mL (40 mL x 5 additions) is collected; amber glass containers are preferred more than plastic. Place the collection bottle under the column, ensuring the tip of the stopcock is near, but not touching the top of the sample bottle (about 5 millimeters [mm]).

2. With a graduated cylinder, slowly pour 40 mL of eluent into the reservoir, lightly tapping the sides of the column to release any air bubbles trapped inside. Wait 15–20 minutes before turning the stopcock to a slow drip (about 1 drop per second). After 10 minutes, open the valve fully to allow any remaining extractant to drain. Plunge any remaining solution out with your gloved hand. Repeat this step four more times, but wait only 5 minutes each time before opening stopcock. Using pH paper, check that the pH of each sample is less than (<) 4. If needed (rarely), add a 0.1 M solution of HCl dropwise until the pH is <4. Store extracts at 4 degree Celsius (°C) until analysis, preferably within 1–2 weeks.

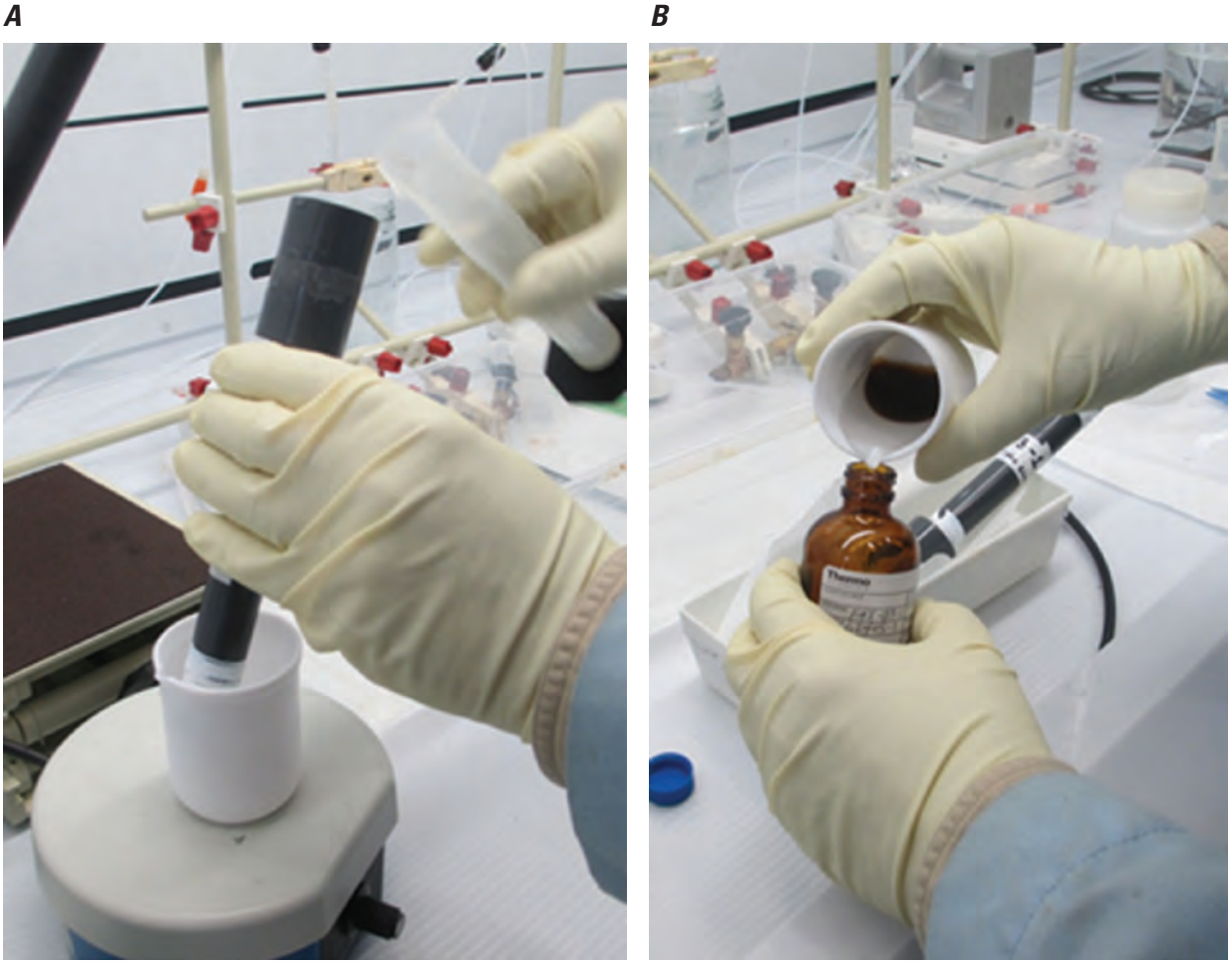

Fig. 1–4. Cation extraction process. *A*, initial addition of a 1 molar solution of potassium chloride to the inverted cation (upper section) column to back-flush resin into the TFE beaker for batch extraction. *B*, decanting the extract into sample bottle.

Cation Extraction (Batch Mode)

1. Prepare a clean U–P DI water-soaked Teflon beaker with a small tetrafluoroethylene (TFE) coated stir bar and place on a magnetic stirring plate. Add 50 mL of the eluent to a clean graduated cylinder. With the upper polyfil plug removed and the top section cleaned with a cotton swab as stated in in the "Column Separation and Extraction" section, carefully invert the upper column above the beaker and slowly pour about 5–10 mL into the bottom of the inverted the column. Gently tap the sides of the column to release any trapped air bubbles (fig. 1–4*A*). Allow the eluent to drip through the bottom polyfil plug and column into the beaker. Continue adding about 10 mL portions of eluent while tapping on the sides of the column. Soon, most of the resin should flush from the column into the beaker. After 50 mL of eluent has been flushed through the column, stir the resin and extract mixture on the stirring plate at moderate rate for 5 minutes. Decant off the eluent into a 125-mL amber glass bottle (fig. 1–4*B*).
2. Similarly, rinse the column into the beaker using a second 50-mL volume of eluent, and stir the resin/extract mixture at a moderate rate for 5 minutes. Decant off the eluent into the 125-mL amber glass bottle to produce a 100-mL extract (fraction 1). Set the column aside.
3. Using a second 125-mL bottle for collection (fraction 2), complete two additional 50-mL batch extractions of the resin. At this juncture (beginning with this third 50-mL volume), the eluent can be added directly to the resin in the beaker (flushing through the column is no longer necessary). Store fractions at 4 °C until analysis for NH_4^+, preferably within 1–2 weeks.
4. If metals are to be analyzed, complete four additional 5-minute batch extractions of the resin using a 3.2 M solution of HNO_3 (do not flush through column). Collect and combine all four 50-mL portions into a 250 mL acid-cleaned polyethylene bottle (fraction 3).

Anion Extraction (Column Mode)

1. Use a 1 M solution of KI and collect 200-mL extract samples in 250-mL polypropylene bottles that have been soaked overnight in U–P DI water. Use new bottles only; do not clean with detergent and ensure there has been no contact with acid.
2. Remove the cap from the top and the plug from the bottom. Attach a clean filling reservoir to the top and a clean stopcock to the bottom.
3. Securely clamp the column to a ringstand. Place a waste sample container underneath. With the stopcock open, rinse the column with 50–100 mL of U–P DI water while periodically tapping on the sides to encourage the resin to settle and to eliminate air pockets. Allow the column to drain completely (about 5 minutes); and then, using a clean gloved hand, push downward on the reservoir while making an airtight seal to plunge out any residual water.
4. Close the stopcock and place collection bottle under the column, ensuring the tip of the stopcock is very near, but not touching the top of the sample bottle (about 5 mm).
5. With a graduated cylinder, slowly pour 40 mL of a 1 M solution of KI eluent into the reservoir, lightly tapping the sides of the column to release any air bubbles trapped inside. Wait 20 minutes before turning the stopcock to a slow drip (about 1 drop per second). After 10 minutes, open the valve fully to allow any remaining eluent to drain. Plunge any remaining solution out with a gloved hand. Repeat this step four more times, but wait only 5 minutes before opening the stopcock.

Ammonium Analysis by Ammonia Probe

1. Prepare NH_4^+ standards of 0.1, 0.5, 1.0, 5.0, and 10.0 milligrams per liter (mg/L) in a 0.1 M solution of KCl. Note carefully if the stock from which these are prepared is expressed as nitrogen (N) or as NH_4^+. Follow the manufacture recommendations for calibration and use of the high performance ammonia (NH_3) electrode. The KCl sample extracts should be diluted 10-fold (2 mL+18 mL of U–P DI water) for analysis. If two bottles were used for extract collection, combine 1 mL from each bottle with 18 mL of U–P DI water to form the sample for analysis.
2. Using the buffer designated specifically for low concentrations, add about 0.4 mL per 20 mL of sample or standard just before completing a measurement. For high concentrations (typically applicable only for the spiked IEC extracts) calibrate the electrode with 1.0, 5.0, and 10 mg/L. For samples, calibrate using the standards of 0.1, 0.5, and 1.0 mg/L. Note that the slope for the low calibration (about -45 millivolt per decade; mv/dec) will be less than for the high one (about -55 mv/dec).
3. Regularly analyze blank solutions and a freshly prepared low-level standard to correct for changes in blank baseline readings and probe response factors.

Troubleshooting

1. Some drift is expected, so regular calibration checks are needed. If the check standard is greater than (>) 10 percent off, try pulling up and down on the electrode wire 2–3 times, which serves to remix the filling solution, and reanalyze a fresh part of the check standard. Note that this will likely temporarily cause a large shift in the reading.
2. If the above procedure does not provide satisfactory results, replace the internal filling solution entirely and reanalyze a fresh check standard.
3. If satisfactory results still cannot be obtained, try rinsing the membrane with methanol to clean the membrane surface because it may have been contaminated by an organic film.
4. Finally, replace the membrane and the internal filling solution and recalibrate the electrode with fresh standards.

Anion Analysis by Ion Chromatography (Dionex ICS–1100)

For an overview on the use of the Dionex ICS–1100, refer to manufacturer manual. Because column anion extracts are in a 1 M KI matrix, the following modifications are needed:

1. Each sample must be diluted at least 10-fold with U–P DI water before analysis.
2. The eluent used is a 9 millimolar (mM) solution of sodium carbonate.
3. Flow is set to 1.0 milliliters per minute and the suppressor to 45 milliamps.
4. Run time is adjusted to cut off just before iodide begins to elute from the column (thus avoiding an extremely large signal from iodide that would swamp the detector).
5. Files for IEC data are stored under the data folder labeled “IEC Data.” The instrumental program is named “Test Carbonate eluent.pgm,” and the quantification method is named “Ion Exchange Fenn.qnt.”

Analysis for Metals

1. If analysis of the cation or anion extract is to be completed by ICP–MS, either the 1 M solution of KCl or 1 M solution of KI matrix must be diluted substantially to avoid problems, typically by at least 40-fold. Only a small number of metals/metalloids are expected to be present in the anion extract, most notably arsenic, molybdenum, and vanadium. For the cation extract, the following approach is recommended.

2. Using an acid rinsed pipet tip, combine 1 mL from each of the two, 100-mL 1 M solution of KCl extract portions (or 2 mL if extract was collected in one bottle) into an acid-cleaned 60-mL polyethylene bottle. Then add 2 mL from the 200-mL 3.2 M solution of HNO_3 extract. Dilute to 40 mL with U–P DI water to give a final matrix of a 0.05 M solution of KCl and a 0.16 M solution of HNO_3 (1 percent volume/volume HNO_3).

3. Analyze the diluted extract by ICP–MS for selected metals or by total quant (TQ) method; however, if the TQ method is used, potassium and chloride must be removed from the list of analyte masses to be monitored.

Calculation of Loads

1. *Snow samples.*—Calculation of the loads for snowpack includes accounting for the number of snow tubes sampled, the area of the snow tube, the total volume of snowpack sampled, and the concentration measured. Loads of major cations or anions are typically presented as kilograms per hectare, whereas loads for trace metals are more conveniently presented as grams per hectare. The calculation is as follows: (measured concentration [in milligrams per liter] x snow volume in liters)/(number of snow tubes x area of one snow tube). As the area of the circle (πr^2) and snow tube r=1.5 inches; the load is calculated first as milligrams per square inch and then kilograms per hectare (kg/ha) from unity values: 1,550 square inches (in^2)/1 square meter (m^2); $1x10^4$ m^2/1 hectare (ha); $1x10^6$ milligrams (mg)/1 kilogram (kg); for example, for a measured concentration of nitrate of 0.50 mg/L where two snow tubes were used to collect a total liquid volume of 0.90 liter (L), the load in kilograms per hectare is: ([0.50]x[0.90])/([2]x[3.14] x[1.5]x[1.5])x(1550x[$1x10^4$/$1x10^6$])=0.4936 kg/ha. The calculation for a metal measured in the snow as 0.50 microgram per liter (µg/L) yields a load of 0.4936 kg/ha. Note that for NH_4^+ and NO_3^-, the loads might be represented better by mass of total nitrogen, rather than mass of by NH_4^+ or NO_3^-, meaning the concentration of NH_4^+ is multiplied by 0.778 (14/18), and the concentration of NO_3^- is multiplied by 0.226 (14/62).

2. *Ion-exchange collectors.*—The calculation is essentially the same as for the snow samples except that the mass collected per unit area is determined from the extract volume (typically 0.2 L for NH_4^+ or anions and 0.4 L for trace metals), and an IEC funnel area of 57 in^2; thus the calculated load for the example above where the concentration of NO_3^- in the IEC extract was 0.50 mg/L is: ([0.50]x[0.2])/([57])x(1,550x[$1x10^4$/$1x10^6$])=0.0272 kg/ha. As indicated above, it should be noted that loads based on total nitrogen might be considered more relevant than loads based on either NH_4^+ or NO_3^-; consequently, the N load from NO_3^- in the example above is equal to (0.226)x(NO_3^- load).

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