

5.2.2.B. Syringe-Filter Procedure for Processing Samples for Analysis of Organic Compounds by DAI LC-MS/MS¹

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This section of chapter 5 of the *National Field Manual for the Collection of Water-Quality Data* (NFM) describes the field procedures for collecting small-volume samples using a syringe-tip filtration method. The samples are sent to the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) for analysis of organic compounds by direct aqueous injection high-performance liquid chromatography/tandem mass spectrometry (DAI LC-MS/MS).²

The DAI LC-MS/MS method was developed specifically for NWQL analytical schedules 2437 (pesticides) and 2440 (pharmaceuticals) and should not be considered transferrable or applicable to other types of samples to be analyzed using methods other than those that use DAI LC-MS/MS or other tandem mass spectrometry methods.

The filter medium required for the filtration procedure must be rinsed and conditioned as described in table 5.2.2.B–1. While some of the filtration equipment can be reused after it is cleaned and otherwise decontaminated, all filter media are non-reusable and are to be discarded after one use (table 5.2.2.B–1).

- ▶ Clean hands/dirty hands (CH/DH) techniques and the associated quality-assurance procedures that are required for inorganic analytes with a concentration at parts per billion or less are recommended for organic analytes as a general good field practice to maintain the integrity of the sample chemistry.
- ▶ Field personnel must wear disposable, powderless gloves (gloves) while processing samples. The gloves must be able to withstand solvents or other chemicals that will be used during sample processing and equipment cleaning; generally, nitrile gloves (elbow length, if available) are recommended. Requirements regarding the selection, preparation, and use of the disposable gloves for USGS water-quality sample collection and handling are described in NFM 2.02 and NFM 4.02.

Compared with the plate-filter procedures described in NFM section 5.2.2.A, use of the syringe-filter technique requires a relatively small volume of sample (10 mL) for analysis. Tandem mass spectrometry, as is used in schedules 2437 and 2440, is more selective than other instruments that typically are used and is less prone to interferences from plastics and other materials, allowing for use of this disposable equipment.

¹ Section 5.2.2.B, in previous versions of this National Field Manual (NFM) chapter, addressed the sample processing procedure for analysis of organonitrogen herbicides (versions 2 through 2.2, dated 4/2002). The method rarely was used and has been deleted from this version of NFM chapter 5.

² Depending on individual project requirements for the collection of multiple samples, the plate-filter and filter-holder assemblies also can be used to collect samples for DAI LC-MS/MS (DAI) analysis. Equipment and supplies used to filter samples for DAI analysis are described in NFM 2, section 2.2.3.B; see figure 2–17. The term DAI LC-MS/MS, as used in this National Field Manual, is synonymous with DAI-HPLC/MS/MS and other variations of acronyms that are used in the literature to refer to the direct aqueous injection high-performance liquid chromatograph/tandem mass spectrometry analytical method.

Table 5.2.2.B-1. Field-conditioning requirements for media used to filter samples for organic-compound analysis.

[mm, millimeter; GF/F, glass-fiber filter; μm , micrometer; PBW, pesticide-grade blank water; mL, milliliter; PFA, perfluoroalkoxy alkane (a fluoropolymer); DAI LC-MS/MS, direct aqueous injection high-performance liquid chromatography/tandem mass spectrometry (synonymous with DAI-HPLC/MS/MS and other variations of those acronyms); LS, laboratory schedule of the USGS National Water Quality Laboratory (NWQL); GMF, graded multi-filter; DOC, dissolved organic carbon; FEP, fluorinated ethylenepropylene; IBW, inorganic blank water; VPBW, nitrogen-purged blank water for volatile organic compounds; DIW, distilled deionized water; WSC, a water science center of the U.S. Geological Survey; L, liter]

Filtration equipment <i>Application</i>	Housing material	Filter media	Filter cleaning and conditioning ¹
Plate-filter assemblies: 142 or 293 mm <i>General trace organic compounds</i>	Stainless steel or aluminum	GF/F (glass-fiber filter) ² : 0.7- μm pore	<ul style="list-style-type: none"> Wet with PBW: <ul style="list-style-type: none"> - 10–20 mL (for 142 mm), or - 50–75 mL (for 293 mm). Rinse and condition filter with 100–125 mL of sample.
Inline PFA filter-holder assembly: 47 mm <i>General trace organic compounds</i>	Teflon [®] PFA	GF/F ² : 0.7- μm pore	<ul style="list-style-type: none"> Wet with 5–10 mL of PBW. Rinse and condition filter with 50 mL of sample.
Disposable syringe-tip filter: 25 mm (DAI LC-MS/MS) <ul style="list-style-type: none"> • <i>LS 2437 Pesticides</i> • <i>LS 2440 Pharmaceuticals</i> 	High-purity polypropylene	GF/F with GMF ³ : 0.7- μm pore	Rinse with 15 mL of sample water or 15 mL of PBW ⁴ to clean and condition the filter.
Pressure filter-holder assem- bly—DOC 25 ⁵ : 25 mm <i>Dissolved and particulate organic carbon</i> ⁶	FEP	GF/F ² : 0.7- μm pore	<ul style="list-style-type: none"> Rinse with 50 mL of IBW, PBW, VPBW, or other certified DOC-free DIW (WSC-produced). Condition filter with 10 mL of sample.
Disposable capsule or disk filter ⁵ <i>Dissolved organic carbon (DOC)</i>	Polypropylene	Thermapor [®] : 0.45- μm pore	<ul style="list-style-type: none"> Using IBW, PBW, VPBW, or other certified DOC-free DIW: <ul style="list-style-type: none"> - Rinse with 2 L for large-capacity capsule, or - Rinse with 50 mL for small-capacity disk. Condition capsule filter with 25 mL and disk filter with 10 mL of sample water.

¹ Filter media (filters) must be prepared as described and discarded after one use.

² Use only glass-fiber filters that have been baked and quality-assured at the USGS National Water Quality Laboratory.

³ Graded multi-filter (GMF): prefilter having a coarse top layer of borosilicate glass microfibers meshed with a fine bottom layer.

⁴ PBW is used only in cases when the quantity of suspended sediment is enough to cause the filter to clog.

⁵ Produced for the USGS by Savillex Corporation, Part 401-61-25-53-60-2. A polysulfone funnel is required when sample will be analyzed for particulate nitrogen and carbon concentrations.

⁶ Disposable capsule and disk filter are illustrated in NFM 2, version 3.1, figure 2–11.

The equipment and procedure used when processing samples for syringe-tip filtration can differ, depending on the manner in which a surface-water or groundwater sample will be collected. Syringe-tip filtration equipment should be obtained from the NWQL-supported national field supply service (NFSS), either as a complete kit (Q765FLD) or as individual components: Q762FLD, syringe-tip filter; Q763FLD, 20-mL syringe; Q764FLD, wide-bore needle; and 20-mL PEST or PHARM borosilicate glass amber vial with septum (refer to NFM 2, ver. 3.1, p. 48–49).

- ▶ For samples collected in a Teflon churn or other noncontaminating wide-mouth compositing container (generally for surface-water applications), the sample is withdrawn using a graduated 20-mL high-purity disposable syringe with a Luer-Lock outlet, a large-bore 1-in. stainless-steel needle with Luer fitting and blunt tip. (Note that if the sample is composited in a precleaned narrow-mouth glass carboy, it needs to be pumped to a precleaned container with an opening wide enough (for example, a 50-mL beaker or 2-oz glass jar) in which the needle attached to the syringe can be submerged).
- ▶ When using a submersible pump to collect a groundwater sample, two sampling options (described below) are provided. For both options the groundwater rate of flow being pumped to land-surface must be reduced to about 50 to 100 mL/min.
 - In Option A, the syringe and bore needle are not needed. The 25-mm syringe-tip filter is connected directly to the outlet of the pump tubing using reducer fittings (table 5.2.2.B–2).
 - In Option B, there is a choice to collect sample water using either the syringe with a bore needle or the syringe without the needle.

Table 5.2.2.B–2. Reducer fittings used for connecting a syringe-tip filter to an inline groundwater sampling pump (used when filtering groundwater samples for DAI LC-MS/MS methods pertaining to pesticides [NWQL schedule 2437] and pharmaceuticals [NWQL schedule 2440]).

[in., inch; PTFE, polytetrafluoroethylene; PFA, perfluoroalkoxy alkane; OD, outer diameter; ETFE, ethylene tetrafluoroethylene]

Vendor	Part number	Description	Number required for assembly
Swagelok ¹	T-400-6-2	Reducer union, 1/4 to 1/8 in., PTFE — OR —	1
Swagelok ¹	T-810-6-2	Reducer union, 1/2 to 1/8 in., PTFE	1
Upchurch Scientific	1641	PFA high purity tubing, 1/8-in. OD	² 1
Upchurch Scientific	XP-315	Flangeless nut, ETFE for 1/8-in. OD tubing (includes ETFE ferrule; or order P-315 flangeless nut and P-300N ferrule separately)	1
Upchurch Scientific	P-623	Union, ETFE, for 1/8-in. OD tubing ³	1
Upchurch Scientific	P-625	Male Luer to 1/4-28 male fitting, ETFE	1

¹The reducer union selected depends on the size of the tubing of the inline groundwater pump system. Examples listed in the table include the reducer fitting for a 1/2-in. tube (figure 5.2.2.B–1) or a 1/4-in. tube (figure 5.2.2.B–2).

²Tubing about 2 to 3 inches in length is needed for each fitting assembly.

³Alternatively, the P-631 union assembly includes two P-300N ferrules and a P-345 nut that connect the 1/8-in. tubing to the union.

When collecting surface-water samples for DAI LC-MS/MS analysis, use the following syringe-filter procedure:

1. Prepare a clean work surface by covering the field bench or table with a fresh sheet of aluminum foil. Wearing nitrile gloves:
 - a. Place the composite sample, waste container, and the plastic bag containing the syringe, large-bore blunt needle, and disposable filter near the clean work surface. Change gloves.
 - b. Open the plastic bag. Remove the syringe, needle, and syringe disk filter from the bag and their wrappings and place them and a sample container (amber glass vial) on clean foil.
2. Homogenize the composited sample following standard USGS water-quality protocols (NFM 5, section 5.1.1.A). Collect samples for inorganic analysis first.

Use the Teflon churn to collect and homogenize a composite sample for DAI LC-MS/MS analysis. This facilitates direct withdrawal of the sample when using the required syringe and bore needle. If samples for inorganic analyses will be taken from the same churn, complete that sampling step first to avoid potential metal contamination of sample water from the bore needle. Alternatively, use separate churns.

3. Clean and condition filtration equipment by rinsing the equipment with sample:
 - a. Attach needle to Luer-Lock fitting on the syringe by twisting the female end of the syringe onto the male Luer-Lock fitting of the needle.
 - Avoid touching the blunt needle that will be inserted into the sample.
 - **Hold only the plastic Luer-Lock fitting of the needle.**
 - b. Submerge the needle in the sample (subsample or Teflon churn) and pull the plunger on the syringe to draw about 15 mL of sample water to rinse the syringe.
 - c. Invert the syringe while carefully removing the needle and placing it on a clean piece of aluminum foil.
 - d. Attach a filter to the syringe by pushing straight down and twisting the open female end of the syringe filter onto the male Luer-Lock fitting on the syringe to provide a secure fit.
 - e. Slowly depress the plunger to force a sample-water rinse through the syringe and filter and into a waste container.
 - f. Remove the filter and place it on the clean foil.
4. Carefully reattach the needle to the syringe and draw 20 mL of sample water into the syringe. Invert the syringe.
 - a. Push the plunger to about the 15 mL (or other whole-number) mark.
 - b. Remove the needle and reattach the rinsed filter, as described in steps 3c and 3d.
5. Invert the syringe-tip filter downward, press the plunger, and half-fill the 20-mL sample container (amber glass vial) with 10 mL of sample filtrate.

- a. These samples are stored in a freezer at the NWQL, requiring that there be sufficient headspace to prevent the glass container from breaking.
 - b. If the samples have high suspended sediment, 15 mL of pesticide-grade blank water (PBW) can be used to clean and rinse the syringe and filter instead of sample (steps 1–3). Then, about 5 mL of sample should be used to condition the syringe and filter after the PBW rinse. Document in field notes any use of PBW (for example, to rinse and condition equipment).
 - c. If the syringe filter medium becomes clogged before a sufficient amount of sample has been filtered, replace it with a new syringe filter and repeat steps 1–5a until the designated volume of filtrate has been collected to half-fill the 20-mL container.
6. After the filtered sample has been collected, cap the container firmly.
 - a. Dry the outside of the container and label it with the appropriate site ID number, date, time, and schedule number.
 - b. Seal the sample in doubled zip-lock bags to prevent contact of the container with melting or melted ice.
 7. Package samples with care in an ice-filled cooler (section 5.5) and ship overnight to the NWQL. Samples must remain chilled at 4 ± 2 °C and unfrozen until received by the NWQL. Refer to NWQL Technical Memorandum 2011.01 (Zogorski, 2011) for shipping procedures for samples containing potential biohazards.
 8. Discard (**do not reuse**) the filter, syringe, and blunt needle (the syringe, however, can be recycled with plastic recyclables). Other reusable items, such as a compositing device or beaker, need to be cleaned in preparation for use at the next site (refer to NFM 3 for cleaning procedures).
 9. Document on field forms and in field notes the filtration procedures used.

When using a submersible pump to collect a groundwater sample for DAI LC-MS/MS analysis, select either Option A or Option B, below:

Samples must be collected and processed in a sample-processing chamber using USGS “clean hands/dirty hands” (CH/DH) techniques. When working in the chamber, use of elbow-length powderless nitrile gloves (instead of wrist-length gloves) is recommended to avoid contamination of samples for pharmaceutical analysis.

Option A: Direct connection between sample line and filter. Neither the disposable syringe nor the bore needle (needle) is used for this procedure.

1. Assemble the processing chamber, installing a clean chamber cover. Prepare a clean work surface and waste container within the chamber. Wearing elbow-length nitrile gloves:
 - a. Place the sample container(s) (amber glass vial), precleaned reducer fittings (table 5.2.2.B–2), and bag containing the filter in the processing chamber.
 - b. Remove the filter from the protective packaging and place on a clean work surface. Change gloves.

2. Using the manifold flow-valve system, follow USGS groundwater sampling protocols as directed in NFM 4, sections 4.2.3 and 4.2.4. Direct the flow of sample to and from the processing chamber and the syringe filter as needed to complete the following steps:
 - a. Connect the precleaned reducer fittings inline to the discharge end of the pump tubing using reducer fittings consisting of a male Luer-Lock connector, a 1/8-in. union, a short length (2 to 3 in.) of 1/8-in. PFA (perfluoroalkoxy alkane) tubing, and a reducer union (table 5.2.2.B–2). The reducer union selected depends on the size of the tubing of the inline groundwater pump system. Examples shown in table 5.2.2.B–2 include reducer fittings for either a 1/2-in. tube (fig. 5.2.2.B–1) or a 1/4-in. tube (fig. 5.2.2.B–2).
 - b. Purge air from the sample tubing, directing sample from the waste (discharge) line to the waste container.
 - c. Reduce the rate of sample flow to about 50 to 100 mL/min.
 - d. Without interrupting sample flow, connect the discharge end of the sample tubing to the syringe filter.
 - e. Allow about 5 mL of sample to rinse and condition the syringe filter, discharging the rinsate to waste.
3. Maintaining a low and uniform rate of flow, collect about 10 mL of sample filtrate in a 20-mL sample vial (container).
 - a. Samples are stored in a freezer at the NWQL and require sufficient headspace to prevent the glass container from breaking.
 - b. If the syringe-filter medium becomes clogged before a sufficient amount of sample has been filtered, replace it with a new syringe filter and repeat steps 2 and 3.
4. After the filtered sample has been collected, cap the vial firmly.
 - a. Dry the outside of the vial.
 - b. Place a label on the vial with the appropriate site ID number, date, time, and schedule number.
 - c. Place the sample vial in a foam sleeve and seal it inside doubled zip-lock bags to prevent contact of the vial with melting or melted ice.
5. Package samples with care in an ice-filled cooler (section 5.5) and ship overnight to the NWQL. Samples must remain chilled at 4 ± 2 °C until they are received by the laboratory. (Samples should not be frozen.) Refer to NWQL Technical Memorandum 2011.01 (Zogorski, 2011) for shipping procedures for samples containing potential biohazards.
6. Discard the syringe filter appropriately (do not reuse). Reusable equipment, such as the sample tubing and reducer fittings used on the filter and the submersible pump must be cleaned in preparation for use at the next site.
7. Document on field forms and in field notes the filtration procedures used.

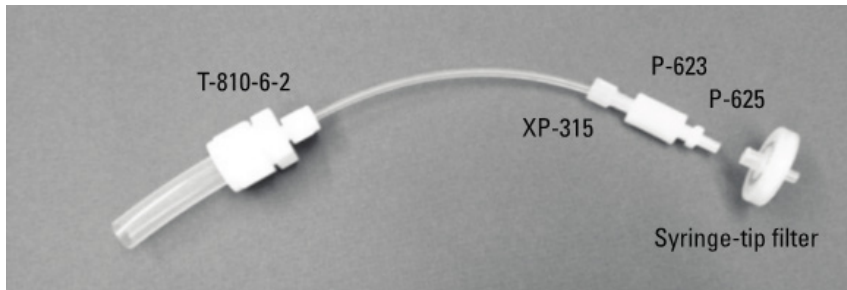


Figure 5.2.2.B-1. Reducer fittings to connect a syringe-tip filter to a 1/2-inch outer diameter tube (see table 5.2.2.B-2).

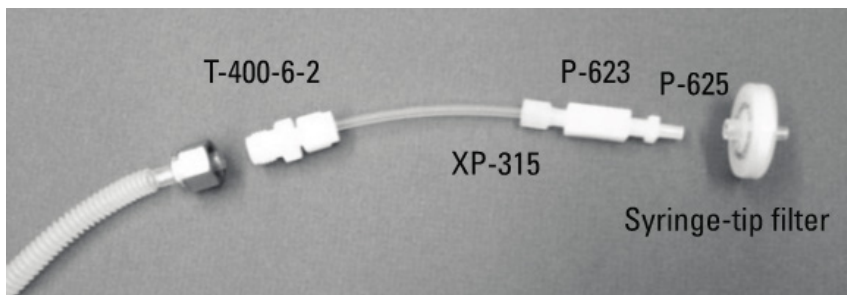


Figure 5.2.2.B-2. Reducer fittings to connect a syringe-tip filter to a 1/4-inch Swagelok nut and 1/2-inch tube (see table 5.2.2.B-2).

Option B: Using the syringe to collect the sample, either with or without the needle (figs. 5.2.2.B-3, 5.2.2.B-4, 5.2.2.B-5).

1. Assemble the processing chamber, installing a clean chamber cover. Prepare a clean work surface and waste container within the chamber. Ensure that the groundwater rate of flow to the processing chamber has been reduced to about 50 to 100 mL/min (refer to step 2 of the Option A groundwater sampling procedure). Select either procedure 2A or 2B below.
2. Syringe procedures:
 - A. *Using the syringe with a needle* (figs. 5.2.2.B-3 and 5.2.2.B-4):
 - a. Wearing nitrile gloves, place the sample container(s) (amber glass vial) in the processing chamber. Remove the syringe, needle, and filter from the protective packaging and place on a clean work surface. Change gloves.
 - b. Attach the bore needle to the syringe and start the flow of groundwater into the chamber. Rinse the exterior of the syringe (or syringe and needle) (fig. 5.2.2.B-3).
 - c. Taking care that the needle does not contact the sample tubing, insert the tip of the needle into the stream of water flowing into the chamber (fig. 5.2.2.B-4). To rinse and condition the syringe filter, syringe and needle, gently pull back on the syringe plunger and collect about 15 to 20 mL of water. (Skip to step 3.)

B. Using the syringe without a needle (figs. 5.2.2.B–3 and 5.2.2.B–5):

- a. Place the sample container(s) in the processing chamber. Remove the syringe and filter from the protective packaging and place on a clean work surface. Change gloves.
- b. Rinse the syringe casing with flowing groundwater. Insert the tip of the syringe into water flowing from the end of the sample tubing.
- c. To rinse and condition the syringe filter and syringe, gently pull back on the syringe plunger and collect about 15 to 20 mL of water.

Note: If the sample in the syringe contains a sizable air bubble, repeat the collection process to reduce the amount of air introduced to the sample.

3. Attach the filter to the syringe, invert, and slowly expel 5 mL of sample to rinse and condition the filter.
4. Holding the syringe-with-filter over a sample container, depress the plunger slowly to half-fill the vial with 10 mL of sample.
5. Cap the container securely and wipe dry. Fill out the sample label, check it for accuracy, and attach the label.
6. Prepare the sample for shipping—Wrap in a protective sleeve and ship on ice overnight to the NWQL.



Figure 5.2.2.B–3. Groundwater flowing into a processing chamber is used to rinse the syringe casing. (Photograph by Michael Manning, U.S. Geological Survey.)



Figure 5.2.2.B-4. Use the bore needle to obtain groundwater for rinsing and conditioning the bore needle and syringe. (Photograph taken inside a sample-processing chamber by Michael Manning, U.S. Geological Survey.)



Figure 5.2.2.B-5. Groundwater flowing directly into a syringe. (Photograph taken inside a sample-processing chamber by Michael Manning, U.S. Geological Survey.)

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