

CHAPTER V

SAMPLING AND ANALYSIS

An effective ground-water sampling and analysis (S & A) program requires a written plan. This plan must include procedures and techniques for sample collection, sample preservation and shipment, analytical procedures and chain of custody control. The plan allows the compliance officer to thoroughly review how the owner/operator has structured the S & A program. Also, comparison of the written plan to field activities will allow the compliance officer to ensure that the owner/operator is, in fact, properly collecting and analyzing ground-water samples.

Elements of the Sampling and Analysis Plan

Specifically, the S & A plan should include information on:

- . Well preparation
- . Sample collection
- . Sample handling and preservation
- . Chain of custody control
- . Analytical procedures
- . Field and laboratory quality assurance/quality control

Well Preparation

The plan should include provisions for measurement of static water level elevations in each well. Measurement of water level elevations on a continuing basis is important to determine if horizontal and vertical flow gradients have changed since initial site characterization. A change in hydrologic conditions may necessitate modification to the design of the owner/operator's ground-water monitoring system. The S & A plan should specify the device to be used for water level measurements as well as the procedure for measuring water levels.

The owner/operator's field measurements should include depth to standing water and total depth of the well to the bottom of the intake screen structure. The measurements should be taken to 0.1 foot. Each well should have a referenced point from which its water level measurement is taken. The reference point should be established in relation to a permanent bench mark and the survey should also note the well location coordinates. The device which is used to detect the water level surface must be sufficiently sensitive that a measurement to 0.1 foot can be obtained reliably. A clean steel tape will usually suffice.

The water standing in a well prior to sampling may not be representative of in-situ ground-water quality. Therefore, the owner/operator should remove the standing water so that water which is representative of the formation can enter the well. The owner/operator's S & A plan should include detailed, step-by-step procedures for evacuating wells. The equipment the owner/operator plans to use to evacuate should also be described.

The procedure the owner/operator should use for well evacuation depends on the yield of the well. When evacuating low yield wells, the owner/operator should evacuate wells to dryness once. If a well cannot be bailed dry, then an amount of water equivalent to three well volumes should be evacuated. The volume to be evacuated should be included in the sampling and analysis plan.

In order to minimize the introduction of contamination into the well positive gas displacement teflon bladder pumps are recommended for purging wells. Teflon or stainless steel 316 bailers are also recommended purging equipment. Where these devices cannot be used, peristaltic pumps, gas-lift pumps, centrifugal pumps, and venturi pumps may be used. Some of these pumps produce volatilization and high pressure differentials, causing variability in the analysis of pH, specific conductance, metals, and volatile organic samples. They are acceptable for purging the wells if sufficient time is allowed to let the water stabilize prior to sampling. Twenty four hours is considered a satisfactory interval before sampling.

When purging equipment must be reused, it should be decontaminated with a tap water wash and a distilled water rinse between wells. Purging equipment which becomes heavily contaminated should be cleaned with a nonphosphate detergent wash, a copious rinse with tap water, and followed by rinsing with isopropanol and distilled water. Clean plastic gloves should be worn by the sampling personnel. A clean plastic sheet should be placed adjacent to or around the well in order to prevent purging equipment and lines from contacting the ground, which in turn could introduce contaminants to the well. Plastic sheet and gloves should be discarded between wells.

Sample Collection

Extraction of well-water samples requires the use of equipment and sample handling in the field that greatly increases the potential for inadvertent sample contamination. Field sampling error greatly exceeds laboratory error. The traces of chemicals being monitored can be lost to the air by agitation or vaporization. They can pass into and out of the water with temperature and pH changes. They can decompose when allowed to stand in the sun. Contamination from the ground surface can pass to hands, to the bottle and then to the sample. Cleanliness and attention to detail will hold these errors to a minimum.

It is important to note that, for a given facility, once a sampling technique has been established it should be repeated for all subsequent samplings. A change in technique may result in a change in the test values.

1. Use only teflon or stainless steel (316) sampling bailers. These may have a bottom valve which facilitates smooth sample release into the bottle, but the bailer may not fit all bottles. A generally useful design has a side opening near the closed top. Care should be taken to see that bailer rope does not touch the sample water.

2. If possible use dedicated samplers for each well. This eliminates cross-contamination, and allows thorough cleaning in the laboratory before the project. If a dedicated sampler is not available the device must be cleaned between wells. This means thoroughly rinsing in distilled water, followed by a thorough rinse in isopropanol and followed by a final rinse in distilled water. If a bailer shows insoluble contamination field cleaning is not recommended.
3. Positive gas displacement teflon bladder pumps may also be used to extract samples.

The owner/operator's S & A plan should specify in detail the devices to be used for sample withdrawal. The plan should state that devices are either dedicated to a specific well or are capable of being fully disassembled and cleaned between wells. Procedures for cleaning the sampling equipment should be included in the plan.

Sampling equipment should be constructed of inert material. Equipment with neoprene fittings, PVC bailers, tygon tubing, silicone rubber bladders, neoprene impellers, polyethylene, and vitron are not acceptable.

Sample Handling and Preservation

1. Dissolved Metals

The well water must not receive preservative before performing a filtration to remove the sediment which may have been stirred up during the purging operation. The sample is either suction filtered in the field, or the bottle is filled to the top without headspace, placed on ice, and filtered in the laboratory immediately after arrival. A 0.45 micron filter disc is used and the filtrate receiving flask must contain the acid preservative. Whichever procedure is adopted should be continued.

The filtrate is tested for the Drinking Water Standard Metals.

2. All sample bottles should be filled to the top, capped with a teflon seal, and be placed on ice immediately after sampling. On arrival at the laboratory they are transferred to a refrigerator. Samples for volatile organic analysis should be filled to the top without headspace. Special vials with septum caps are available for this purpose.

Table V-1 is a list of preservatives and holding times.

3. pH and Specific Conductance should be performed immediately after collection if possible. The calibration and procedure should be recorded and continued at each sampling project. If a sample is returned to the laboratory, it should be tested immediately on arrival and this alternate procedure should be recorded and repeated at each sampling project.
4. Sample delivery to the laboratory should be in the shortest possible time after collection. If delay is incurred this should be entered in the field log book along with the time increment.

TABLE V-1
Perservation Procedures and Holding Times

<u>Parameter</u>	<u>Recommended Container</u>	<u>Preservative Indicators of Ground-water Contamination</u>	<u>Holding Time</u>	<u>Volume Required For One Analysis</u>
pH	T, P, G	Field determined	None	25 ml
Specific conductance	T, P, G	Field determined	None	100 ml
TOC	G, T-lined cap	Cool 4°C HCl to pH 2	28 days	4 x 15 ml
TOX	G, amber, T-lined septa or caps	Cool 4°C, add 1 ml of 1.1M sodium sulfite	7 days	4 x 15 ml
Chloride	T, P, G	4°C	28 days	50 ml
Arsenic	T, P	<u>Total Metals</u> Field Acidified to pH 2 with HNO ₃	6 months	1,000 ml
Barium				
Cadmium			6 months	1,000 ml
Chromium				
Lead		<u>Dissolved Metals</u>		
Mercury		1. Field filtration if possible		
Selenium		2. Acidify the filtrate to pH 2 with HNO ₃		
Silver				
Fluoride	T, P	Cool 4°C	28 days	300 ml
Nitrate/Nitrite	T, P, G	4°C/H ₂ SO ₄ to pH 2	14 days	1,000 ml
Volatile Organics	G, T-lined septa or caps	Cool 4°C	7-14 days (extract in 5 days)	60 ml
Pesticides	G	Cool 4°C	(5 days to extract) 30 days	2,000 ml
Extractable Organics	G	Cool 4°C	30 days (extract in 5 days)	
Cyanide	P, G	Cool 4°C NaOH to pH 12 0.6g ascorbic acid (see method)	14 days*	500 ml
Oil & Grease	G only	Cool 4°C, H ₂ SO ₄ to pH 2	28 days	100 ml
Phenols	G	Cool 4°C, H ₂ SO ₄ to pH 2	(5 days to extract) 30 days	500

*Unless sulfide is present, - then 24 hours (see lab method)

P = polyethylene

G = glass

T = fluorocarbon resins (Teflon, PTFE, FEP, etc.)

5. Blanks and Background

A distilled water blank should be carried to the field and put through the entire sampling procedure. If positives are found, this will alert the collector to field sampling error. (See Quality Assurance)

In certain situations it may be good procedure to sample neighborhood well water to establish a background concentration for parameters of interest, in addition to installed up-gradient wells.

Chain of Custody

Custody and protection of samples is an important legal consideration. As few people as possible should handle the samples. The sampler is personally responsible for collected samples, and must be able to attest to the integrity of samples until transfer. If the samples are placed in a vehicle, it must be kept locked. Any ice chest must be locked or located in a place which is locked, and having access only by responsible officials.

A chain-of-custody form documents the handling of samples from the moment of collection until testing. It contains the facility name, date of sampling and name of the collector. Samples must have consecutive ID numbers which are kept in a sampling log book. The ID number is entered on the chain-of-study along with a word description of each sample. Note that several bottles collected for different parameters will have the same ID number if they come from one sampling point. Each transfer of custody is recorded on the chain-of-custody with an appropriate signature, date and time.

If the samples are to be shipped they must be sealed. The driver for the delivery service must sign the custody form and a bill of lading must be secured.

Analytical Procedures

The S&A plan should identify the method that will be used to test for each specific parameter or constituent. The plan should specify a method in EPA Manual SW-846 Ed. III, EPA Manual 600/4-79-020, or a method approved by the Division. Any planned deviation should be justified and submitted for approval by the Division prior to use

Records of ground-water analyses should include the methods used (by number), the extraction date, and date of actual analysis. Data from samples that are not analyzed within recommended holding times should be considered suspect.

Field and Laboratory Quality Assurance/Quality Control

It is the responsibility of the owner/operator to ensure the reliability of the analytical data being gathered during the monitoring program. The S & A plan must explicitly describe what will be done in the field. An example procedure is provided in Appendix II as a guide to good technique which can be adapted as required for the situation at hand.

A field blank should be part of each sampling event. Distilled water is taken to the site, and handled like a sample. It is poured into a bailer, and sample bottles filled using identical technique. Analysis of the blank alerts the sampler to technical error. The blank test results are not used to correct the sample results, but are reported as-is. If the contaminant levels in the blank are within an order of magnitude of the groundwater sample results, the wells should be resampled.

Many owner/operators employ commercial laboratories to conduct analyses of groundwater samples. In these cases it is the owner/operator's responsibility to ensure that the laboratory of choice is exercising a proper QA/QC program as described in the S & A plan. The approved EPA test methods contain within them the requirement to run a spiked sample to determine percent recovery. This should be a part of the lab report. Additional quality control such as method blanks and duplicates are also described in the test method and should be included in the laboratory work agreement. The laboratory QA program should be a part of the S & A Plan. Quality assurance procedures are time consuming and increase the cost of testing, but the facility will be regulated based on the results and it is to their advantage to employ the best qualified laboratory.

All field instruments that the owner/operator will use should be calibrated prior to field use and recalibrated in the field before measuring each sample. The owner/operator's S&A plan should describe a program for ensuring proper calibration of field instruments. Other QA/QC practices such as sampling equipment decontamination procedures and chain-of-custody procedures should also be described in the owner/operator's S&A plan.

Analysis of Results

1. In order to determine whether the groundwater is receiving contamination from the site it is necessary to compare the test results with the background test results. Several inherent variabilities must be considered:
 - a. The sampling technique will vary somewhat from event to event even under ideal conditions.
 - b. The aquifer will contain a certain quantity of elements.
 - c. The laboratory test itself can vary slightly.

A method must be used that shows significant deviation beyond the inherent deviation. A statistical analysis using the Student's t-test is presently approved by EPA for this purpose. While several approaches are possible the details are beyond the scope of this manual and the reader is referred to several texts on statistics listed in the references. The EPA approved Behrens-Fischer method is included as a step by step guide in Appendix I. The facility should submit the statistical method for EPD approval in the S & A plan.

2. A single laboratory result may be very accurate or considerably in error depending on a number of factors:
 - a. Interferences in the sample.
 - b. Contamination picked up during sample preparation.
 - c. The skill of the analyst.
 - d. The time delay.
 - e. The instrument calibration.
 - f. The field sampling error for that day.

If a particular test result shows 100 ppm for example, and the lower detectable limit is 1 ppm, it can be assumed that contamination exists and repeat testing may be at the discretion of the facility. However, most cases are considerably closer to the lower detectable limit of the test, and verification becomes essential.

A properly verified result is accompanied by the following:

- a. A duplicate sample result.
- b. A spiked sample result.
- c. A blank result.
- d. A set of calibration standards run to establish instrument response.

If all are performed with good results, the facility and the Division can be assured that the sample result is representative. At the very least a sample should be spiked with a known quantity of the sought for constituent to determine percent recovery. With good recoveries no interferences are present in the water to suppress or enhance the response of the instrument.

The Division recommends that a second sampling project be undertaken whenever a downgradient result gives cause for alarm.