

APPENDIX C

GROUNDWATER SAMPLING PROTOCOL

Prior to collecting groundwater samples from monitoring wells, approximately three to four well casing volumes of groundwater will be removed from each well using a positive displacement piston pump set at least 10 feet above the bottom of the well.

During pumping, temperature, pH, electrical conductivity and total dissolved solids will be measured periodically using field calibrated instrumentation. Groundwater samples will be collected when parameters have stabilized in three consecutive readings. If the field parameters do not stabilize before three casing volumes have been removed, additional groundwater will be bailed until the parameters stabilize. Total water volume removed will be approximated using a 5-gallon bucket or inline flowmeter. In the event the well goes dry before three casing volumes have been removed or before parameters have stabilized, the well will be allowed to recover to at least 80 percent of the static water level before the sample is collected.

Field parameter data will be collected using instruments calibrated to standard solutions at the beginning of each sampling day. Calibration results will be recorded in the field daily report. Deviations in calibration will be noted. Field parameter data will be checked and validated by a Certified Hydrogeologist.

Groundwater samples will be collected following pumping using a Teflon or stainless steel bailer that has been cleaned using a Liqui-Nox soap (or equivalent) solution wash and potable and distilled water rinses. Samples will be decanted from the bailer into properly labeled, laboratory-prepared sample containers. Each sample label will include the well number, project number, date and time sampled, analytical test, preservative (if any) and sampler's initials. Samples will be sealed in sealable plastic bags and placed in a field cooler with ice immediately after collection.

For QA/QC purposes, duplicate samples will be collected in the field from two wells during each sampling event. These samples will be submitted to the laboratory "blind" with a fictitious well

designation so the repeatability of the analytical results can be objectively evaluated. Duplicate samples will be collected from the same bailer whenever possible to maximize the representativeness of the analytical results. The label given the duplicate sample will be noted on standard sampling forms and/or in the field daily notes to enable later identification and comparison.

If sampling bailers are used in multiple wells, one equipment blank per day of sampling will be collected to ensure the effectiveness of bailer cleaning between wells. The blank sample will consist of distilled water decanted from a cleaned bailer into a laboratory prepared sample container. The blank sample will be collected between sampling of wells.

All groundwater samples will be submitted to a California Department of Health Services certified laboratory under chain-of-custody protocol within 24 hours of collection.

ASTM STANDARDS ON GROUND WATER AND VADOSE ZONE INVESTIGATIONS

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Standard Guide for Sampling Groundwater Monitoring Wells¹

This standard is issued under the fixed designation D 4448; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers procedures for obtaining valid, representative samples from groundwater monitoring wells. The scope is limited to sampling and "in the field" preservation and does not include well location, depth, well development, design and construction, screening, or analytical procedures.

1.2 This guide is only intended to provide a review of many of the most commonly used methods for sampling groundwater quality monitoring wells and is not intended to serve as a groundwater monitoring plan for any specific application. Because of the large and ever increasing number of options available, no single guide can be viewed as comprehensive. The practitioner must make every effort to ensure that the methods used, whether or not they are addressed in this guide, are adequate to satisfy the monitoring objectives at each site.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Summary of Guide

2.1 The equipment and procedures used for sampling a monitoring well depend on many factors. These include, but are not limited to, the design and construction of the well, rate of groundwater flow, and the chemical species of interest. Sampling procedures will be different if analyzing for trace organics, volatiles, oxidizable species, or trace metals is needed. This guide considers all of these factors by discussing equipment and procedure options at each stage of the sampling sequence. For ease of organization, the sampling process can be divided into three steps: well flushing, sample withdrawal, and field preparation of samples.

2.2 Monitoring wells must be flushed prior to sampling so that the groundwater is sampled, not the stagnant water in the well casing. If the well casing can be emptied, this may be done although it may be necessary to avoid oxygen contact with the groundwater. If the well cannot be emptied, procedures must be established to demonstrate that the sample represents groundwater. Monitoring an indicative parameter such as pH during flushing is desirable if such a parameter can be identified.

2.3 The types of species that are to be monitored as well as the concentration levels are prime factors for selecting sampling devices (1, 2).² The sampling device and all materials and devices the water contacts must be constructed of materials that will not introduce contaminants or alter the analyte chemically in any way.

2.4 The method of sample withdrawal can vary with the parameters of interest. The ideal sampling scheme would employ a completely inert material, would not subject the sample to negative pressure and only moderate positive pressure, would not expose the sample to the atmosphere, or preferably, any other gaseous atmosphere before conveying it to the sample container or flow cell for on-site analysis.

2.5 The degree and type of effort and care that goes into a sampling program is always dependent on the chemical species of interest and the concentration levels of interest. As the concentration level of the chemical species of analytical interest decreases, the work and precautions necessary for sampling are increased. Therefore, the sampling objective must clearly be defined ahead of time. For example, to prepare equipment for sampling for mg/L (ppm) levels of Total Organic Carbon (TOC) in water is about an order of magnitude easier than preparing to sample for $\mu\text{g/L}$ (ppb) levels of a trace organic like benzene. The specific precautions to be taken in preparing to sample for trace organics are different from those to be taken in sampling for trace metals. No final Environmental Protection Agency (EPA) protocol is available for sampling of trace organics. A short guidance manual, (3) and an EPA document (4) concerning monitoring well sampling, including considerations for trace organics are available.

2.6 Care must be taken not to cross contaminate samples or monitoring wells with sampling or pumping devices or materials. All samples, sampling devices, and containers must be protected from the environment when not in use. Water level measurements should be made before the well is flushed. Oxidation-reduction potential, pH, dissolved oxygen, and temperature measurements and filtration should all be performed on the sample in the field, if possible. All but temperature measurement must be done prior to any significant atmospheric exposure, if possible.

2.7 The sampling procedures must be well planned and all sample containers must be prepared and labeled prior to going to the field.

3. Significance and Use

3.1 The quality of groundwater has become an issue of national concern. Groundwater monitoring wells are one of

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² The boldface numbers in parentheses refer to a list of references at the end of this guide.

TABLE 1 Typical Container and Preservation Requirements for a Ground-Water Monitoring Program

Sample and Measurement	Volume Required (mL)	Container P—Polyethylene G—Glass	Preservative	Maximum Holding Time
Metals As/Ba/Cd/Cr/Fe Pb/Se/ Ag/Mn/Na	1000–2000	P/G (special acid cleaning)	high purity nitric acid to pH <2	6 months
Mercury	200–300	P/G (special acid cleaning)	high purity nitric acid to pH <2 +0.05 % K ₂ Cr ₂ O ₇	28 days
Radioactivity alpha/beta/radium	4000	P/G (special acid cleaning)	high purity nitric acid to pH <2	6 months
Phenolics	500–1000	G	cool, 4°C H ₂ SO ₄ to pH <2	28 days
Miscellaneous	1000–2000	P	cool, 4°C	28 days
Fluoride	300–500	P		28 days
Chloride	50–200	P/G		28 days
Sulfate	100–500	P/G		48 hours
Nitrate	100–250	P/G		6 h
Coliform	100	P/G		on site/24 h
Conductivity	100	P/G		on site/6 h
pH	100	P/G		48 h
Turbidity	100	P/G		
Total organic carbon (TOC)	25–100	P/G	cool, 4°C or cool, 4°C HCl or H ₂ SO ₄ to pH <2	24 h 28 days
Pesticides, herbicides and total organic halogen (TOX)	1000–4000	G/TFE-fluorocarbon lined cap solvent rinsed	cool, 4°C	7 days/extraction +30 days/analysis
Extractable organics	1000–2000	G/TFE-fluorocarbon-lined cap solvent rinsed	cool, 4°C	7 days/extraction +30 days/analysis
Organic purgeables acrolein/acrylonitrile	25–120	G/vial TFE-fluorocarbon-lined septum	cool, 4°C	14 days 3 days

the more important tools for evaluating the quality of groundwater, delineating contamination plumes, and establishing the integrity of hazardous material management facilities.

3.2 The goal in sampling groundwater monitoring wells is to obtain samples that are truly representative of the aquifer or groundwater in question. This guide discusses the advantages and disadvantages of various well flushing, sample withdrawal, and sample preservation techniques. It reviews the parameters that need to be considered in developing a valid sampling plan.

4. Well Flushing (Purging)

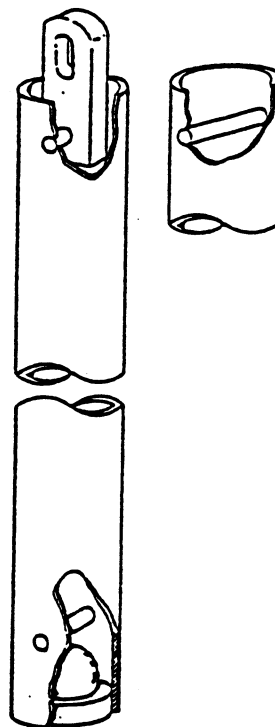
4.1 Water that stands within a monitoring well for a long period of time may become unrepresentative of formation water because chemical or biochemical change may cause water quality alterations and even if it is unchanged from the time it entered the well, the stored water may not be representative of formation water at the time of sampling, or both. Because the representativeness of stored water is questionable, it should be excluded from samples collected from a monitoring well.

4.2 The surest way of accomplishing this objective is to remove all stored water from the casing prior to sampling. Research with a tracer in a full scale model 2 in. PVC well (5) indicates that pumping 5 to 10 times the volume of the well via an inlet near the free water surface is sufficient to remove all the stored water in the casing. The volume of the well may

be calculated to include the well screen and any gravel pack if natural flow through these is deemed insufficient to keep them flushed out.

4.3 In deep or large diameter wells having a volume of water so large as to make removal of all the water impractical, it may be feasible to lower a pump or pump inlet to some point well below the water surface, purge only the volume below that point then withdraw the sample from a deeper level. Research indicates this approach should avoid most contamination associated with stored water (5, 6, 7). Sealing the casing above the purge point with a packer may make this approach more dependable by preventing migration of stored water from above. But the packer must be above the top of the screened zone, or stagnant water from above the packer will flow into the purged zone through the well's gravel/sand pack.

4.4 In low yielding wells, the only practical way to remove all standing water may be to empty the casing. Since it is not always possible to remove all water, it may be advisable to let the well recover (refill) and empty it again at least once. If introduction of oxygen into the aquifer may be of concern, it would be best not to uncover the screen when performing the above procedures. The main disadvantage of methods designed to remove all the stored water is that large volumes may need to be pumped in certain instances. The main advantage is that the potential for contamination of samples with stored water is minimized.



NOTE—Taken from Ref (15).

FIG. 1 Single Check Valve Bailer

4.5 Another approach to well flushing is to monitor one or more indicator parameters such as pH, temperature, or conductivity and consider the well to be flushed when the indicator(s) no longer change. The advantage of this method is that pumping can be done from any location within the casing and the volume of stored water present has no direct bearing on the volume of water that must be pumped. Obviously, in a low yielding well, the well may be emptied before the parameters stabilize. A disadvantage of this approach is that there is no assurance in all situations that the stabilized parameters represent formation water. If significant drawdown has occurred, water from some distance away may be pulled into the screen, causing a steady parameter reading but not a representative reading. Also, a suitable indicator parameter and means of continuously measuring it in the field must be available.

4.6 Gibb (4, 8) has described a time-drawdown approach using a knowledge of the well hydraulics to predict the percentage of stored water entering a pump inlet near the top of the screen at any time after flushing begins. Samples are taken when the percentage is acceptably low. As before, the advantage is that well volume has no direct effect in the duration of pumping. A current knowledge of the well's hydraulic characteristics is necessary to employ this approach. Downward migration of stored water due to effects other than drawdown (for example density differences) is not accounted for in this approach.

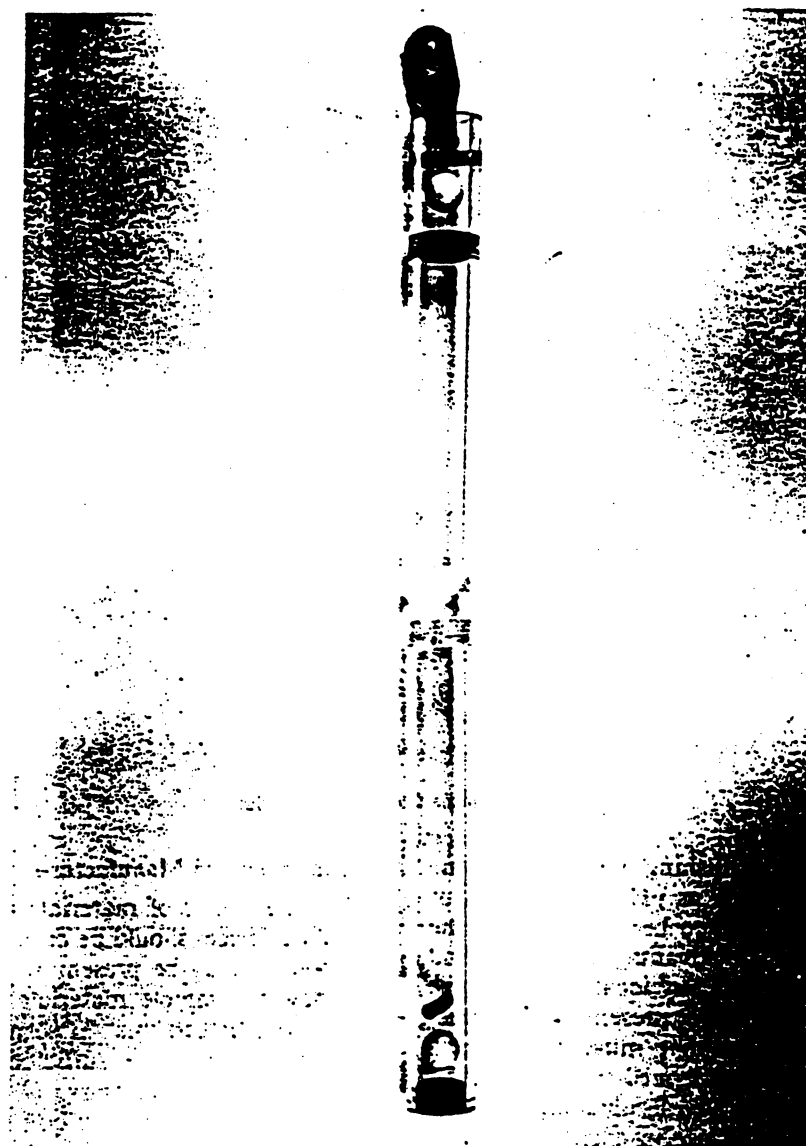
4.7 In any flushing approach, a withdrawal rate that minimizes drawdown while satisfying time constraints should be used. Excessive drawdown distorts the natural flow patterns around a well and can cause contaminants that were not present originally to be drawn into the well.

5. Materials and Manufacture

5.1 The choice of materials used in the construction of sampling devices should be based upon a knowledge of what compounds may be present in the sampling environment and how the sample materials may interact via leaching, adsorption, or catalysis. In some situations, PVC or some other plastic may be sufficient. In others, an all glass apparatus may be necessary.

5.2 Most analytical protocols suggest that the devices used in sampling and storing samples for trace organics analysis ($\mu\text{g/L}$ levels) must be constructed of glass or TFE-fluorocarbon resin, or both. One suggestion advanced by the EPA is that the monitoring well be constructed so that only TFE-fluorocarbon tubing be used in that portion of the sampling well that extends from a few feet above the water table to the bottom of the borehole. (3, 5) Although this type of well casing is now commercially available, PVC well casings are currently the most popular. If adhesives are avoided, PVC well casings are acceptable in many cases although their use may still lead to some problems if trace organics are of concern. At present, the type of background presented by PVC and interactions occurring between PVC and groundwater are not well understood. Tin, in the form of an organotin stabilizer added to PVC, may enter samples taken from PVC casing. (9)

5.3 Since the most significant problem encountered in trace organics sampling, results from the use of PVC adhesives in monitoring well construction, threaded joints might avoid the problem (3, 5). Milligram per litre (parts per million) levels of compounds such as tetrahydrofuran, methyl-ethyl-ketone, and toluene are found to leach into



NOTE—Taken from Ref (17).

FIG. 2 Acrylic Point Source Bailer

groundwater samples from monitoring well casings sealed with PVC solvent cement. Pollutant phthalate esters (8, 10) are often found in water samples at ppb levels; the EPA has found them on occasion at ppm levels in their samples. The ubiquitous presence of these phthalate esters is unexplained, except to say that they may be leached from plastic pipes, sampling devices, and containers.

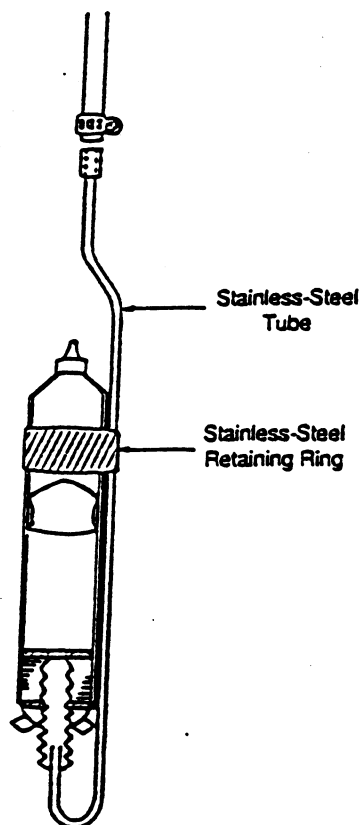
5.4 TFE-fluorocarbon resins are highly inert and have sufficient mechanical strength to permit fabrication of sampling devices and well casings. Molded parts are exposed to high temperature during fabrication which destroys any organic contaminants. The evolution of fluorinated compounds can occur during fabrication, will cease rapidly, and does not occur afterwards unless the resin is heated to its melting point.

5.5 Extruded tubing of TFE-fluorocarbon for sampling may contain surface traces of an organic solvent extrusion aid. This can be removed easily by the fabricator and, once

removed by flushing, should not affect the sample. TFE-fluorocarbon FEP and TFE-fluorocarbon PFA resins do not require this extrusion aid and may be suitable for sample tubing as well. Unsintered thread-sealant tape of TFE-fluorocarbon is available in an "oxygen service" grade and contains no extrusion aid and lubricant.

5.6 Louneman, et al. (11) alludes to problems caused by a lubricating oil used during TFE-fluorocarbon tubing extrusion. This reference also presents evidence that a fluorinated ethylene-propylene copolymer adsorbed acetone to a degree that later caused contamination of a gas sample.

5.7 Glass and stainless steel are two other materials generally considered inert in aqueous environments. Glass is probably among the best choices though it is not inconceivable it could adsorb some constituents as well as release other contaminants (for example, Na, silicate, and Fe). Of course, glass sampling equipment must be handled carefully in the field. Stainless steel is strongly and easily machined to



Note—Taken from Ref (21).

FIG. 3 Schematic of the Inverted Syringe Sampler

fabricate equipment. Unfortunately, it is not totally immune to corrosion that could release metallic contaminants. Stainless steel contains various alloying metals, some of these (for example Ni) are commonly used as catalysts for various reactions. The alloyed constituents of some stainless steels can be solubilized by the pitting action of nonoxidizing anions such as chloride, fluoride, and in some instances sulfate, over a range of pH conditions. Aluminum, titanium, polyethylene, and other corrosion resistant materials have been proposed by some as acceptable materials, depending on groundwater quality and the constituents of interest.

5.8 Where temporarily installed sampling equipment is used, the sampling device that is chosen should be non-plastic (unless TFE-fluorocarbon), cleanable of trace organics, and must be cleaned between each monitoring well use in order to avoid cross-contamination of wells and samples. The only way to ensure that the device is indeed "clean" and acceptable is to analyze laboratory water blanks and field water blanks that have been soaked in and passed through the sampling device to check for the background levels that may result from the sampling materials or from field conditions. Thus, all samplings for trace materials should be accompanied by samples which represent the field background (if possible), the sampling equipment background, and the laboratory background.

5.9 Additional samples are often taken in the field and spiked (spiked-field samples) in order to verify that the sample handling procedures are valid. The American Chem-

ical Society's committee on environmental improvement has published guidelines for data acquisition and data evaluation which should be useful in such environmental evaluations (10, 12).

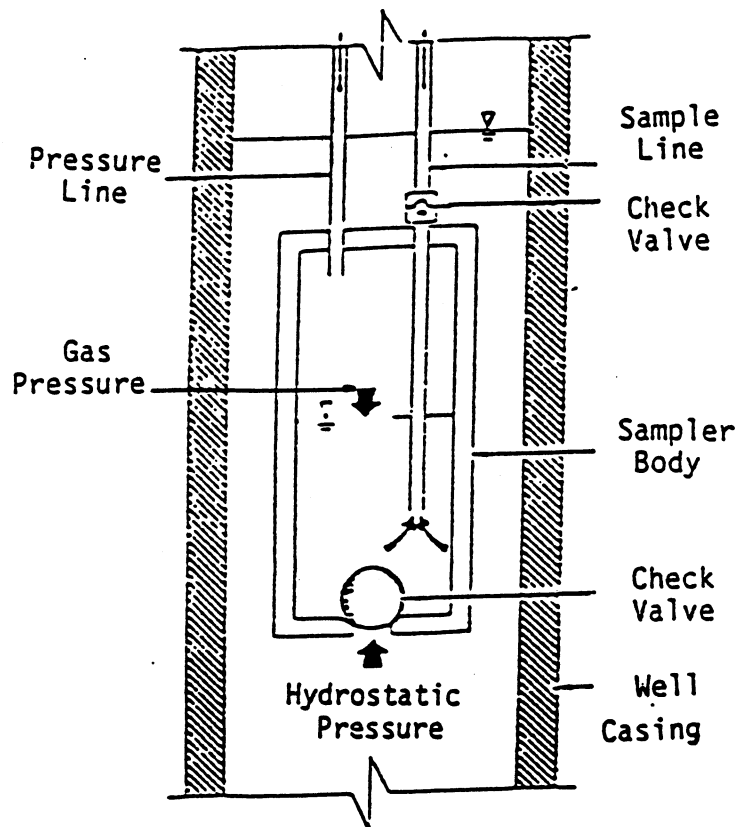
6. Sampling Equipment

6.1 There is a fairly large choice of equipment presently available for groundwater sampling from single screened wells and well clusters. The sampling devices can be categorized into the following eight basic types.

6.1.1 Down-Hole Collection Devices:

6.1.1.1 Bailers, messenger bailers, or thief samplers (13, 14) are examples of down-hole devices that probably provide valid samples once the well has been flushed. They are not practical for removal of large volumes of water. These devices can be constructed in various shapes and sizes from a variety of materials. They do not subject the sample to pressure extremes.

6.1.1.2 Bailers do expose part of the sample to the atmosphere during withdrawal. Bailers used for sampling of volatile organic compounds should have a sample cock or draft valve in or near the bottom of the sampler allowing withdrawal of a sample from the well below the exposed surface of the water or the first few inches of the sample should be discarded. Suspension lines for bailers and other samplers should be kept off the ground and free of other contaminating materials that could be carried into the well. Down-hole devices are not very practical for use in deep



NOTE—Taken from Ref (5).

FIG. 4 The Principal of Gas Displacement Pumping

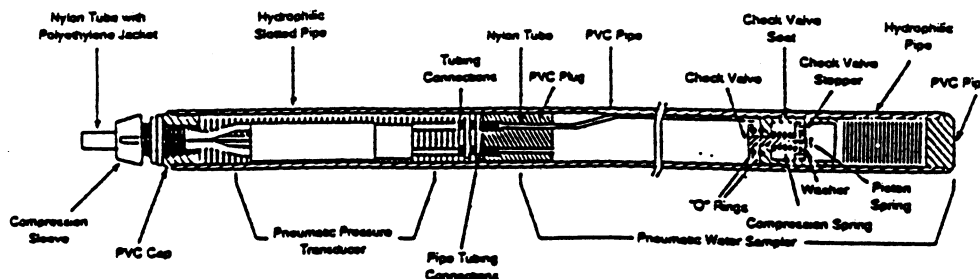
wells. However, potential sample oxidation during transfer of the sample into a collection vessel and time constraints for lowering and retrieval for deep sampling are the primary disadvantages.

6.1.1.3 Three down-hole devices are the single and double check valve bailers and thief samplers. A schematic of a single check valve unit is illustrated in Fig. 1. The bailer may be threaded in the middle so that additional lengths of blank casing may be added to increase the sampling volume. IFE-fluorocarbon or PVC are the most common materials used for construction (15).

6.1.1.4 In operation, the single check valve bailer is lowered into the well, water enters the chamber through the bottom, and the weight of the water column closes the check

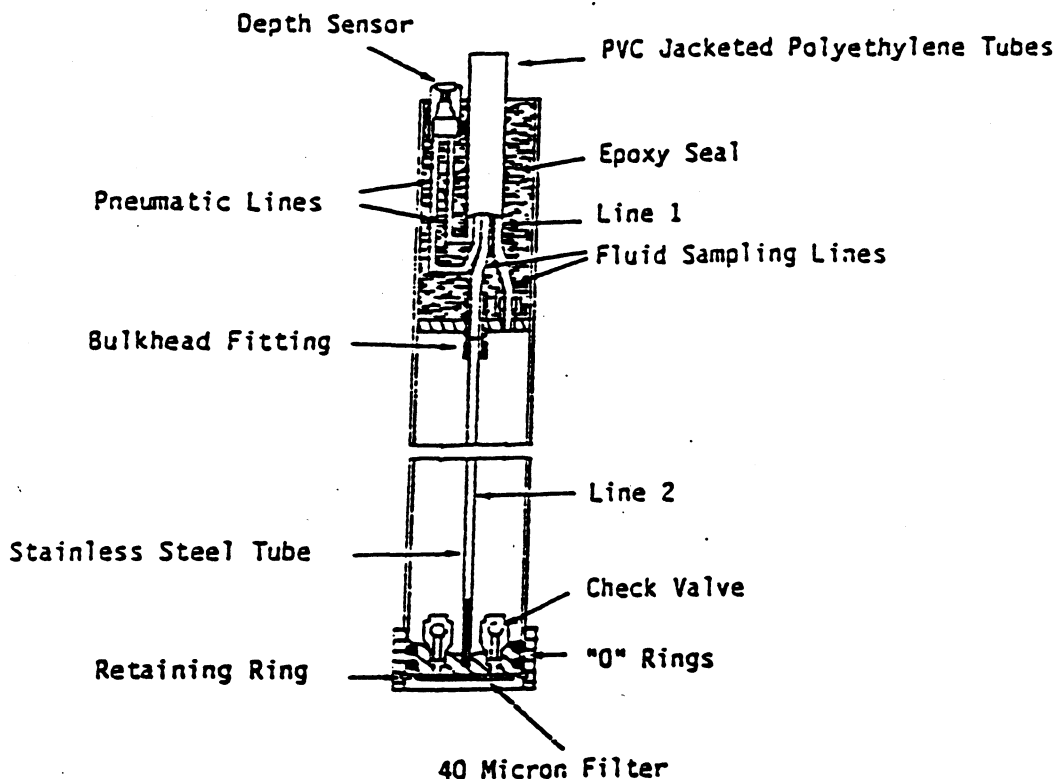
valve upon bailer retrieval. The specific gravity of the ball should be about 1.4 to 2.0 so that the ball almost sits on the check valve seat during chamber filling. Upon bailer withdrawal, the ball will immediately seat without any samples loss through the check valve. A similar technique involves lowering a sealed sample container within a weighted bottle into the well. The stopper is then pulled from the bottle via a line and the entire assembly is retrieved upon filling of the container (14, 16).

6.1.1.5 A double check valve bailer allows point source sampling at a specific depth (15, 17). An example is shown in Fig. 2. In this double check valve design, water flows through the sample chamber as the unit is lowered. A venturi tapered inlet and outlet ensures that water passes freely through the



NOTE—Taken from Ref (41).

FIG. 5 Pneumatic Water Sampler With Internal Transducer



Note—Taken from Ref (42).

FIG. 6 Pneumatic Sampler With Externally Mounted Transducer

unit. When a depth where the sample is to be collected is reached, the unit is retrieved. Because the difference between each ball and check valve seat is maintained by a pin that blocks vertical movement of the check ball, both check valves close simultaneously upon retrieval. A drainage pin is placed into the bottom of the bailer to drain the sample directly into a collection vessel to reduce the possibility of air oxidation. The acrylic model in Fig. 2 is threaded at the midsection allowing the addition of threaded casing to increase the sampling volume.

6.1.1.6 Another approach for obtaining point source samples employs a weighted messenger or pneumatic change to "trip" plugs at either end of an open tube (for example, tube water sampler or thief sampler) to close the chamber (18). Foerst, Kemmerer, and Bacon samplers are of this variety (14, 17, 19). A simple and inexpensive pneumatic sampler was recently described by Gillham (20). The device (Fig. 3) consists of a disposable 50 mL plastic syringe modified by sawing off the plunger and the finger grips. The syringe is then attached to a gas-line by means of a rubber stopper assembly. The gas-line extends to the surface, and is used to drive the stem-less plunger, and to raise and lower the syringe into the hole. When the gas-line is pressurized, the rubber plunger is held at the tip of the syringe. The sampler is then lowered into the installation, and when the desired depth is reached, the pressure in the gas-line is reduced to atmospheric (or slightly less) and water enters the syringe. The sampler is then retrieved from the installation and the syringe detached from the gas-line. After the tip is sealed, the syringe is used as a short-term storage container. A number

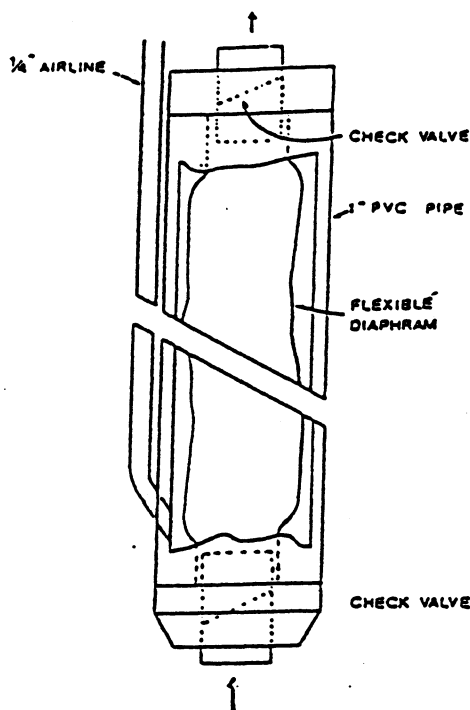
of thief or messenger devices are available in various materials and shapes.

6.1.2 Suction Lift Pumps:

6.1.2.1 Three types of suction lift pumps are the direct line, centrifugal, and peristaltic. A major disadvantage of any suction pump is that it is limited in its ability to raise water by the head available from atmospheric pressure. Thus, if the surface of the water is more than about 25 ft below the pump, water may not be withdrawn. The theoretical suction limit is about 34 ft, but most suction pumps are capable of maintaining a water lift of only 25 ft or less.

6.1.2.2 Many suction pumps draw the water through some sort of volute in which impellers, pistons, or other devices operate to induce a vacuum. Such pumps are probably unacceptable for most sampling purposes because they are usually constructed of common materials such as brass or mild steel and may expose samples to lubricants. They often induce very low pressures around rotating vanes or other such parts such that degassing or even cavitation may occur. They can mix air with the sample via small leaks in the casing, and they are difficult to adequately clean between uses. Such pumps are acceptable for purging of wells, but should not generally be used for sampling.

6.1.2.3 One exception to the above statements is a peristaltic pump. A peristaltic pump is a self-priming, low volume suction pump which consists of a rotor with ball bearing rollers (21). Flexible tubing is inserted around the pump rotor and squeezed by heads as they revolve in a circular pattern around the rotor. One end of the tubing is placed into the well while the other end can be connected



NOTE—Taken from Ref (4).

FIG. 7 Bladder Pump

directly to a receiving vessel. As the rotor moves, a reduced pressure is created in the well tubing and an increased pressure (<40 psi) on the tube leaving the rotor head. A drive shaft connected to the rotor head can be extended so that multiple rotor heads can be attached to a single drive shaft.

6.1.2.4 The peristaltic pump moves the liquid totally within the sample tube. No part of the pump contacts the liquid. The sample may still be degassed (cavitation is unlikely) but the problems due to contact with the pump mechanism are eliminated. Peristaltic pumps do require a fairly flexible section of tubing within the pumphead itself. A section of silicone tubing is commonly used within the peristaltic pumphead, but other types of tubing can be used particularly for the sections extending into the well or from the pump to the receiving container. The National Council of the Paper Industry for Air and Stream Improvement (22) recommends using medical grade silicone tubing for organic sampling purposes as the standard grade uses an organic vulcanizing agent which has been shown to leach into samples. Medical grade silicone tube is, however, limited to use over a restricted range of ambient temperatures. Various manufacturers offer tubing lined with TFE-fluorocarbon or Viton³ for use with their pumps. Gibb (1, 8) found little difference between samples withdrawn by a peristaltic pump and those taken by a bailer.

6.1.2.5 A direct method of collecting a sample by suction consists of lowering one end of a length of plastic tubing into the well or piezometer. The opposite end of the tubing is connected to a two way stopper bottle and a hand held or

mechanical vacuum pump is attached to a second tubing leaving the bottle. A check valve is attached between the two lines to maintain a constant vacuum control. A sample can then be drawn directly into the collection vessel without contacting the pump mechanism (5, 23, 24).

6.1.2.6 A centrifugal pump can be attached to a length of plastic tubing that is lowered into the well. A foot valve is usually attached to the end of the well tubing to assist in priming the tube. The maximum lift is about 4.6 m (15 ft) for such an arrangement (23, 25, 26).

6.1.2.7 Suction pump approaches offer a simple sample retrieval method for shallow monitoring. The direct line method is extremely portable though considerable oxidation and mixing may occur during collection. A centrifugal pump will agitate the sample to an even greater degree although pumping rates of 19 to 151 Lpm (5 to 40 gpm) can be attained. A peristaltic pump provides a lower sampling rate with less agitation than the other two pumps. The withdrawal rate of peristaltic pumps can be carefully regulated by adjustment of the rotor head revolution.

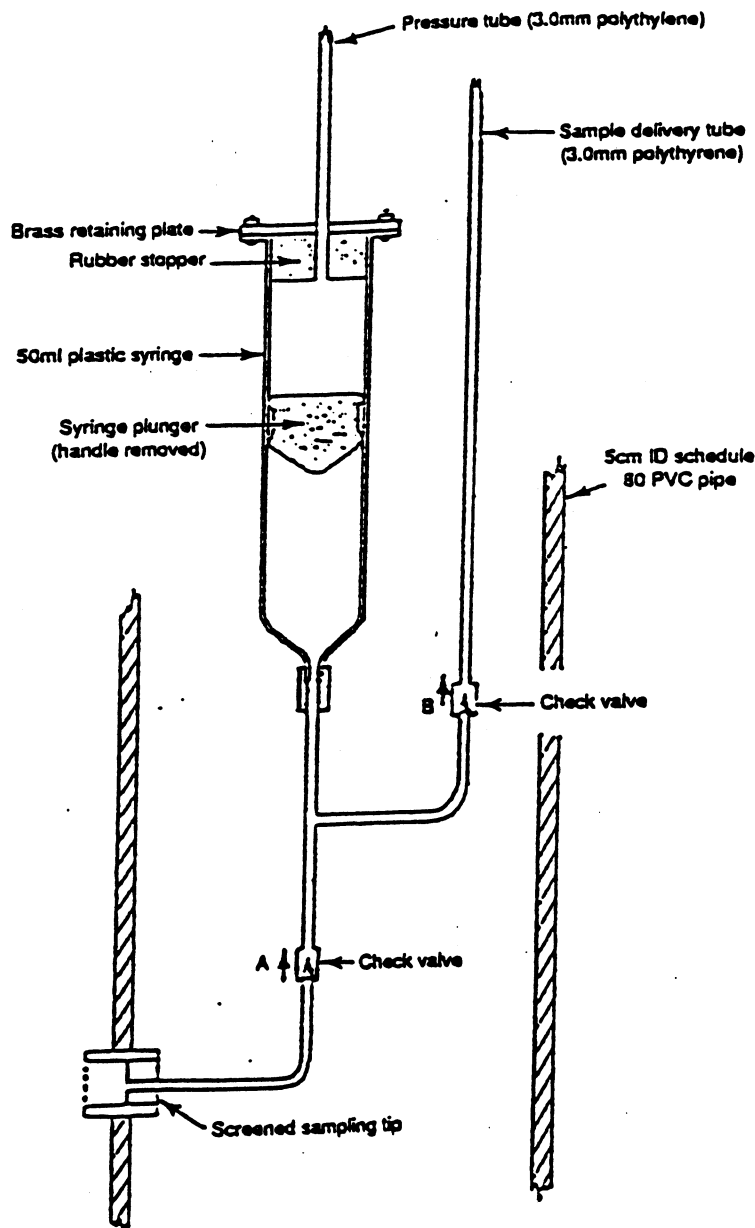
6.1.2.8 All three systems can be specially designed so that the water sample contacts only the TFE fluorocarbon or silicone tubing prior to sample bottle entry. Separate tubing is recommended for each well or piezometer sampled.

6.1.3 Electric Submersible Pumps:

6.1.3.1 A submersible pump consists of a sealed electric motor that powers a piston or helical single thread worm at a high rpm. Water is brought to the surface through an access tube. Such pumps have been used in the water well industry for years and many designs exist (5, 26).

6.1.3.2 Submersible pumps provide relatively high discharge rates for water withdrawal at depths beyond suction

³ Viton is a trademark of E. I. du Pont de Nemours & Co., Wilmington, DE 19898 and has been found suitable for this purpose.



NOTE—Taken from Ref (48).

FIG. 8 Positive Displacement Syringe Pump

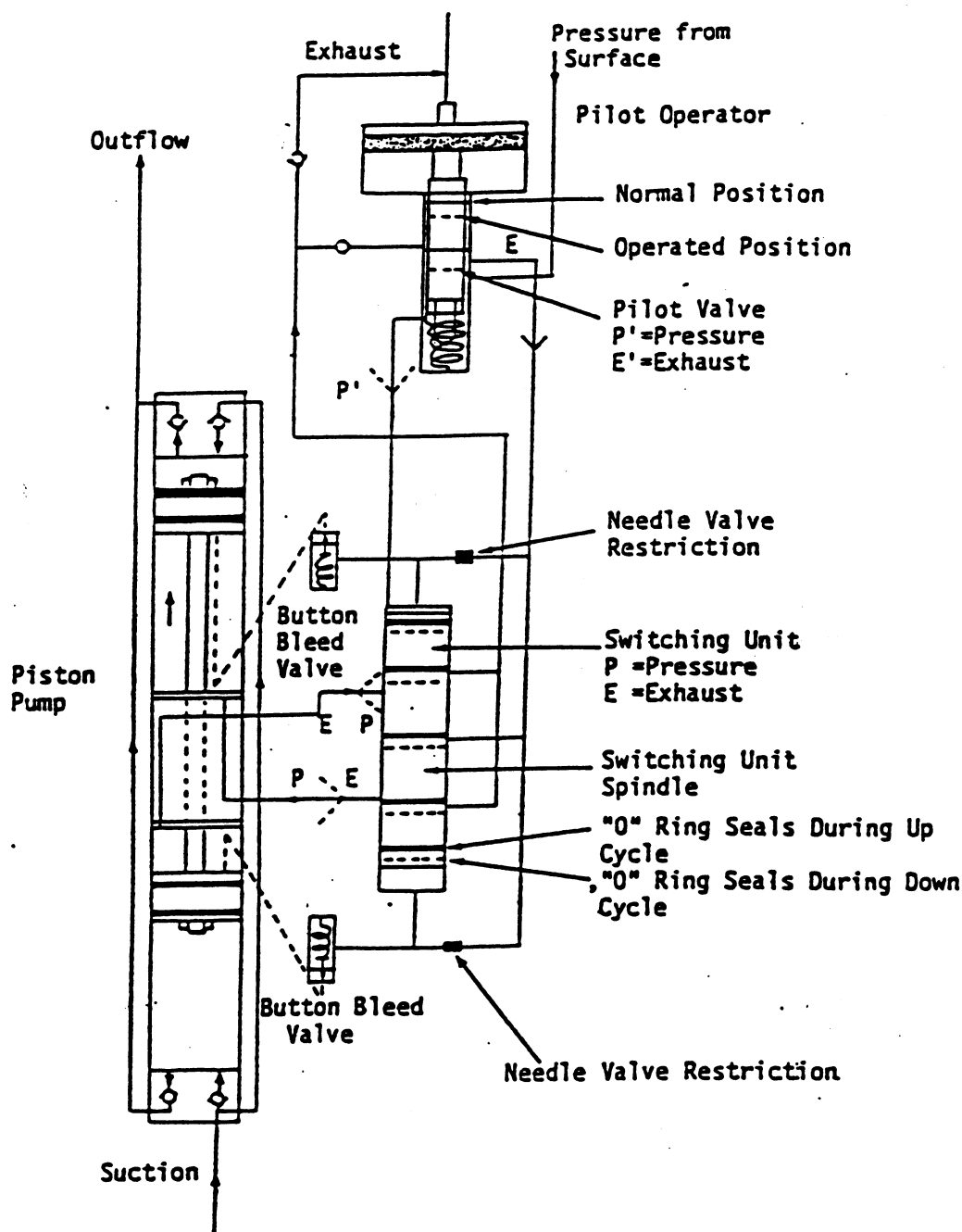
lift capabilities. A battery operated unit 3.6 cm (1.4 in.) in diameter and with a 4.5 Lpm (1.2 gpm) flow rate at 33.5 m (110 ft) has been developed (27). Another submersible pump has an outer diameter of 11.4 cm (4.5 in.) and can pump water from 91 m (300 ft). Pumping rates vary up to 53.0 Lpm (14 gpm) depending upon the depth of the pump (28).

6.1.3.3 A submersible pump provides higher extraction rates than many other methods. Considerable sample agitation results, however, in the well and in the collection tube during transport. The possibility of introducing trace metals into the sample from pump materials also exists. Steam cleaning of the unit followed by rinsing with unchlorinated, deionized water is suggested between sampling when analysis for organics in the parts per million (ppm) or parts per billion (ppb) range is required (29).

6.1.4 Gas-Lift Pumps:

6.1.4.1 Gas-lift pumps use compressed air to bring a water sample to the surface. Water is forced up an eductor pipe that may be the outer casing or a smaller diameter pipe inserted into the well annulus below the water level (30, 31).

6.1.4.2 A similar principle is used for a unit that consists of a small diameter plastic tube perforated in the lower end. This tube is placed within another tube of slightly larger diameter. Compressed air is injected into the inner tube; the air bubbles through the perforations, thereby lifting the water sample via the annulus between the outer and inner tubing (32). In practice, the eductor line should be submerged to a depth equal to 60 % of the total submerged eductor length during pumping (26). A 60 % ratio is considered optimal although a 30 % submergence ratio is adequate.



NOTE—Taken from Ref (49).

FIG. 9 Gas Driven Piston Pump

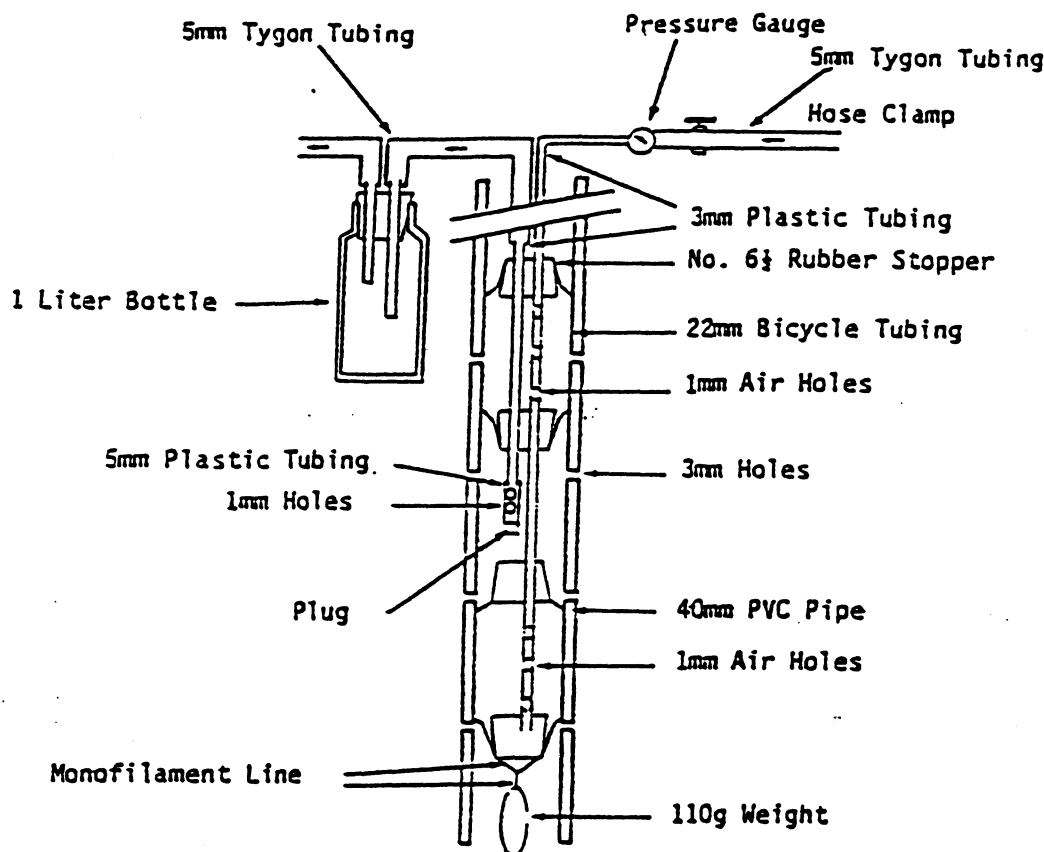
6.1.4.3 The source of compressed gas may be a hand pump for depths generally less than 7.6 m (25 ft). For greater depths, air compressors, pressurized air bottles, and air compressed from an automobile engine have been used.

6.1.4.4 As already mentioned, gas-lift methods result in considerable sample agitation and mixing within the well, and cannot be used for samples which will be tested for volatile organics. The eductor pipe or weighted plastic tubing is a potential source of sample contamination. In addition, Webb (8) uncovered difficulties in sampling for inorganics. These difficulties were attributed to changes in redox, pH,

and species transformation due to solubility constant changes resulting from stripping, oxidation, and pressure changes.

6.1.5 Gas Displacement Pumps:

6.1.5.1 Gas displacement or gas drive pumps are distinguished from gas-lift pumps by the method of sample transport. Gas displacement pumps force a discrete column of water to the surface via mechanical lift without extensive mixing of the pressurized gas and water as occurs with air-lift equipment. The principle is shown schematically in Fig. 4. Water fills the chamber. A positive pressure is applied to the



NOTE—Taken from Ref (53).

FIG. 10 Packer Pump Arrangement

gas line closing the sampler check valve and forcing water up the sample line. By removing the pressure the cycle can be repeated. Vacuum can also be used in conjunction with the gas (30). The device can be permanently installed in the well (33, 34, 35) or lowered into the well (36, 37).

6.1.5.2 A more complicated two stage design constructed of glass with check valves made of TFE-fluorocarbon has been constructed (38, 39). The unit was designed specifically for sample testing for trace level organics. Continuous flow rates up to 2.3 Lpm (0.6 gpm) are possible with a 5.1 cm (2 in.) diameter unit.

6.1.5.3 Gas displacement pumps have also been developed with multiple functions. The water sample in Fig. 5 provides piezometric data measurements with an internally mounted transducer (40). A sample with its transducer exposed externally for piezometric measurements is illustrated in Fig. 6 (41). The sensor can activate the gas source at the surface to cause sample chamber pressurization at the predetermined depth. Another design can be used as a water sampler or as a tool for injecting brine or other tracers into a well (42).

6.1.5.4 Gas displacement pumps offer reasonable potential for preserving sample integrity because little of the driving gas comes in contact with the sample as the sample is conveyed to the surface by a positive pressure. There is, however, a potential loss of dissolved gases or contamination from the driving gas and the housing materials.

6.1.6 Bladder Pumps:

6.1.6.1 Bladder pumps, also referred to as gas-operated squeeze pumps, consist of a flexible membrane enclosed by a rigid housing. Water enters the membrane through a check valve in the vessel bottom; compressed gas injected into the cavity between the housing and bladder forces the sample through a check valve at the top of the membrane and into a discharge line (Fig. 7). Water is prevented from re-entering the bladder by the top check valve. The process is repeated to cycle the water to the surface. Samples taken from depths of 30.5 m (100 ft) have been reported.

6.1.6.2 A variety of design modifications and materials are available (43, 44). Bladder materials include neoprene, rubber, ethylene propylene terpolymer (E.P.T.), nitrile, and the fluorocarbon Viton.³ A bladder made of TFE-fluorocarbon is also under development (45). Automated sampling systems have been developed to control the time between pressurization cycles (46).

6.1.6.3 Bladder pumps provide an adaptable sampling tool due primarily to the number of bladder shapes that are feasible. These devices have a distinct advantage over gas displacement pumps in that there is no contact with the driving gas. Disadvantages include the large gas volumes required, low pumping rates, and potential contamination from many of the bladder materials, the rigid housing, or both.

6.1.7 Gas Driven Piston Pumps:

6.1.7.1 A simple and inexpensive example of a gas driven piston pump is a syringe pump (47). The pump (Fig. 8) is constructed from a 50 mL plastic syringe with plunger stem removed. The device is connected to a gas line to the surface and the sample passes through a check valve arrangement to a sampling container at the surface. By successively applying positive and negative pressure to the gas-line, the plunger is activated driving water to the surface.

6.1.7.2 A double piston pump powered by compressed air is illustrated in Fig. 9. Pressurized gas enters the chamber between the pistons; the alternating chamber pressurization activates the piston which allows water entry during the suction stroke of the piston and forces the sample to the surface during the pressure stroke (48). Pumping rates between 9.5 and 30.3 L/hr (2.5 to 8. gal/hr) have been reported from 30.5 m (100 ft). Depths in excess of 457 m (1500 ft) are possible.

6.1.7.3 The gas piston pump provides continuous sample withdrawal at depths greater than is possible with most other approaches. Nevertheless, contribution of trace elements from the stainless steel and brass is a potential problem and the quantity of gas used is significant.

6.1.8 *Packer Pump Arrangement:*

6.1.8.1 A packer pump arrangement provides a means by which two expandable "packers" isolate a sampling unit between two packers within a well. Since the hydraulic or pneumatic activated packers are wedged against the casing wall or screen, the sampling unit will obtain water samples only from the isolated well portion. The packers are deflated for vertical movement within the well and inflated when the desired depth is attained. Submersible, gas lift, and suction pumps can be used for sampling. The packers are usually constructed from some type of rubber or rubber compound (48, 49, 50, 51). A packer pump unit consisting of a vacuum sampler positioned between two packers is illustrated in Fig. 10 (52).

6.1.8.2 A packer assembly allows the isolation of discrete sampling points within a well. A number of different samplers can be situated between the packers depending upon the analytical specifications for sample testing. Vertical movement of water outside the well casing during sampling is possible with packer pumps but depends upon the pumping rate and subsequent disturbance. Deterioration of the expandable materials will occur with time with the increased possibility of undesirable organic contaminants contributing to the water sample.

7. Sample Containers and Preservation

7.1 Complete and unequivocal preservation of samples, whether domestic wastewater, industrial wastes, or natural waters, is practically impossible. At best, preservation techniques only retard the chemical and biological changes that inevitably continue after the sample is removed from the source. Therefore, insuring the timely analysis of a sample should be one of the foremost considerations in the sampling plan schedule. Methods of preservation are somewhat limited and are intended to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce the volatility of constituents. Preservation methods are generally limited to pH control, chemical addition, refrigeration and freezing. For water samples, immediate

refrigeration just above freezing (4°C in wet ice) is often the best preservation technique available, but it is not the only measure nor is it applicable in all cases. There may be special cases where it might be prudent to include a recording thermometer in the sample shipment to verify the maximum and minimum temperature to which the samples were exposed. Inexpensive devices for this purpose are available.

7.2 All bottles and containers must be specially pre-cleaned, pre-labelled, and organized in ice-chests (isolating samples and sampling equipment from the environment) before one goes into the field. Otherwise, in any comprehensive program utter chaos usually develops in the field or laboratory. The time in the field is very valuable and should be spent on taking field notes, measurements, and in documenting samples, not on labelling and organizing samples. Therefore, the sampling plan should include clear instructions to the sampling personnel concerning the information required in the field data record logbook (notebook), the information needed on container labels for identification, the chain-of-custody protocols, and the methods for preparing field blanks and spiked samples. Example of detailed plans and documentation procedures have been published (14, 53).

7.3 The exact requirements for the volumes of sample needed and the number of containers to use may vary from laboratory to laboratory. This will depend on the specific analyses to be performed, the concentration levels of interest, and the individual laboratory protocols. The manager of the sampling program should make no assumptions about the laboratory analyses. He should discuss the analytical requirements of the sampling program in detail with the laboratory coordinator beforehand. This is especially the case since some analyses and preservation measures must be performed at the laboratory as soon as possible after the samples arrive. Thus, appropriate arrangements must be made.

7.4 There are a number of excellent references available which list the containers and preservation techniques appropriate for water and soils (13, 14, 50, 54, 55, 56). The "Handbook for Sampling and Sample Preservation of Water and Wastewater" is an excellent reference and perhaps the most comprehensive one (14). Some of this information is summarized in Table 1.

7.5 Sample containers for trace organic samples require special cleaning and handling considerations (57). The sample container for purgeable organics consist of a screw-cap vial (25 to 125 mL) fitted with a TFE-fluorocarbon faced silicone septum. The vial is sealed in the laboratory immediately after cleaning and is only opened in the field just prior to pouring sample into it. The water sample then must be sealed into the vial headspace free (no air bubbles) and immediately cooled (4°C) for shipment. Multiple samples (usually about four taken from one large sample container) are taken because leakage of containers may cause losses, may allow air to enter the containers, and may cause erroneous analysis of some constituents. Also, some analyses are best conducted on independent protected samples.

7.6 The purgeable samples must be analyzed by the laboratory within 14 days after collection, unless they are to be analyzed for acrolein or acrylonitrile (in which case they are to be analyzed within 3 days). For samples for solvent extractions (extractable organics-base neutrals, acids and

pesticides), the sample bottles are narrow mouth, screw cap quart bottles or half-gallon bottles that have been pre-cleaned, rinsed with the extracting organic solvent and oven dried at 105°C for at least 1 h. These bottles must be sealed with TFE-fluorocarbon lined caps (Note). Samples for organic extraction must be extracted within 7 days and analyzed within 30 days after extraction. Special pre-cleaned, solvent rinsed and oven-dried stainless steel beakers (one for each monitoring well) may be used for transferring samples from the sampling device to the sample containers.

NOTE—When collecting samples, the bottles should not be overfilled or prerinsed with sample before filling because oil and other materials may remain in the bottle. This can cause erroneously high results.

7.7 For a number of groundwater parameters, the most meaningful measurements are those made in the field at the time of sample collection or at least at an on-site laboratory. These include the water level in the well and parameters that sometimes can change rapidly with storage. A discussion of the various techniques for measuring the water level in the well is contained in a NCASI publication (5) and detailed procedures are outlined in a U.S. Geological Survey publication (58). Although a discussion of these techniques is beyond the scope of this guide, it is important to point out that accurate measurements must be made before a well is flushed or only after it has had sufficient time to recover. Parameters that can change rapidly with storage include specific conductance, pH, turbidity, redox potential, dissolved oxygen, and temperature. For some of the other

parameters, the emphasis in groundwater monitoring is on the concentration of each specific dissolved component, not the total concentration of each. Samples for these types of measurements should be filtered through 0.45 µm membrane filters ideally in the field or possibly at an on-site laboratory as soon as possible. Analyses often requiring filtered samples include all metals, radioactivity parameters, total organic carbon, dissolved orthophosphate (if needed), and total dissolved phosphorous (if needed) (13, 14). If metals are to be analyzed, filter the sample prior to acid preservation. For TOC organics, the filter material should be tested to assure that it does not contribute to the TOC. The type or size of the filter to be used is not well understood. However, if results of metal, TOC or other parameters that could be effected by solids are to be compared, the same filtering procedure must be used in each case. Repeated analytical results should state whether the samples were filtered and how they were filtered.

7.8 Shipment and receipt of samples must be coordinated with the laboratory to minimize time in transit. All samples for organic analysis (and many other parameters), should arrive at the laboratory within one day after it is shipped and be maintained at about 4°C with wet ice. The best way to get them to the laboratory in good condition is to send them in sturdy insulated ice chests (coolers) equipped with bottle dividers. 24-h courier service is recommended, if personal delivery service is not practical.

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