Collecting and Preserving Waste and Wastewater Samples for Analysis

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Waste handling systems as part of livestock production layouts are being developed and used to protect the environment.

One part of waste management is sampling and analyzing the waste and wastewater to know what you have. Information from samples can be valuable for properly operating the system.

If results of analyses of waste samples are to be meaningful, then the sample collection and preservation must be done properly.

Procedures outlined in this guide are for field sampling from livestock operations. They are not meant as a guide to sampling for scientific research, which in many instances requires specific and highly sophisticated sampling methods.

Collecting a sample

Getting meaningful data from samples depends greatly on proper collection. Improperly collected samples may yield information with little usefulness. The laboratory analyst must work with material brought in and can't magically abstract results from a sample that was improperly collected and stored.

Specific sampling recommendations for all situations can't be given because of the variety of local conditions that may exist at any one site. A few basic procedures help, but most proper sampling techniques result from proper judgment.

The sample must truly represent the existing conditions. How collecting is done depends on the specific analyses to be made from the sample, the expected results from the analyses, and the type of operation being sampled.

For example, if an oxidation ditch is being sampled to determine the solids content, the sample must be obtained from a point within the ditch where the contents are being thoroughly mixed. This ensures a true representation of the overall solids content.

To ensure representative sampling, take several samples from different locations. This provides more accurate analytical results and will also permit any irregularity to be discovered. For example, a minimum of three samples should be taken from various locations from a livestock lagoon.

Samples should not be collected from places not representing the major portion of the contents. Avoid narrow arms of lagoons, dead spots in pits and tanks and areas of heavier-than-normal loadings.

For most analyses performed on livestock wastes, take a sample of about 1 pint (500 milliliters). Use a wide-mouth bottle having a diameter of at least 1.4 inches (35 millimeters) at the mouth.

Tightly seal the sample container immediately after collection.

The bottle can be of glass or plastic. Plastic is preferred because it is less likely to be broken. If preservatives are used, add them to the bottle prior to collecting the sample.

Each sample should be labeled or tagged for identification. Include the date, time of collection, name of collector and location. Also, other information that may be needed for later correlation include weather conditions, water level, flow rate and waste loading. Sampling points should be fixed by detailed description maps, stakes or markers.

Because biological or chemical changes may occur within the sample following collection, some analyses must be performed at the time the sample is collected. These include temperature, pH, and tests for oxygen, carbon dioxide and hydrogen sulfide. Getting help from a person experienced in such sampling is recommended.

Preserving a sample

Various methods of preservation and their application to waste samples are explained in Table 1. The most practical and reliable method of preservation in the field is refrigeration. Equipment is usually available and it doesn't interfere with analysis. Putting samples in ice and keeping them there until they are submitted to the laboratory will preserve them well enough for most tests.

Table 1
Preservatives used to reduce changes in the sample[1]

Preservative	Action	Applicable to
Mercuric chloride ($HgCl_2$)	Bacterial inhibitor	Nitrogen forms, phosphorus forms

Preservative	Action	Applicable to
Nitric acid (HNO_3)	Metals solvents, prevents precipitation	All metals
Sulfuric acid (H_2SO_4)	Bacterial inhibitor	Organic samples (COD, organic carbon, nitrogen, etc.)
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration or freezing	Bacterial inhibitor	Acid — alkalinity, organic materials, BOD, color, odor, organic orthophosphate, organic nitrogen, carbon, etc., biological organisms (coliforms, etc.)

[1]Table data from "Methods for Chemical Analysis of Water and Wastes," Environmental Protection Agency, Water Quality Office, Analytical Control Laboratory, Cincinnati, Ohio.

Proper preservation can only retard the chemical and biological changes in the sample. Complete preservation is impossible in most cases. Changes occur rapidly once the waste has been collected.

Biological action involving nitrogen and phosphorus cycles are the most notable changes in waste samples.

Organic nitrogen is released as ammonia nitrogen when bacteria decompose organic matter. Ammonia is lost as a gas or converted to nitrites, which are rapidly oxidized to nitrates by bacteria. Nitrates can be reduced back to ammonia by bacterial reduction. This cycle continues unless retarded by a bacterial inhibitor.

The nitrogen balance can be held in check for a maximum of seven days by adding sulfuric acid and refrigerating the sample.

In determining phosphorus content, preservation is not necessary if total phosphorus is to be determined. However, if orthophosphate (PO_4) is to be determined, the sample should be preserved by adding 40 milligrams of mercuric chloride ($HgCl_2$) per liter (about 1.05 quarts). Organic phosphorus is converted to orthophosphate by bacterial decomposition.

The waste sample should be immediately cooled to 40 degrees Fahrenheit (about 4 degrees Celsius). This refrigeration will maintain biochemical oxygen demand.

Certain ions may change chemically in a waste sample. Metal ions may be precipitated as insoluble salts or absorbed onto the wall of the collection bottle, while other ions may change form. Preservation is accomplished by refrigerating or by adding nitric acid.

Dissolved gases (oxygen, carbon dioxide, hydrogen sulfide), pH, and temperature can change within minutes after collection. There are no practical methods of preserving these. Analyses for them should be performed at the collection site.

Recommended preservatives and maximum holding periods for most determinations made on wastes and waste waters are summarized in Table 2.

Table 2
Sample preservation

Analyses	**Preservative**	**Maximum holding period**
Total carbon	4 degrees Celsius	7 days
Organic carbon	2 milliliters sulfuric acid per liter	7 days
Total phosphorus	2 milliliters sulfuric acid per liter	7 days
Ortho phosphate	40 milligrams mercuric chloride per liter or 2 milliliters sulfuric acid per liter	7 days
Total Kjeldahl nitrogen	4 degrees Celsius and 0.8 milliliter sulfuric acid per liter	unstable
Nitrate (NO_3^-)	0.8 milliliter sulfuric acid per liter	7 days
Nitrate (NO_2^-)	0.8 milliliter sulfuric acid per liter	7 days
Ammonia-N	0.8 milliliter sulfuric acid per liter	7 days
Fecal coliform	4 degrees Celsius	6 hours
Total coliform	4 degrees Celsius	6 hours
Fecal streptococci	4 degrees Celsius	6 hours
Biochemical oxygen demand	4 degrees Celsius	6 hours
Chemical oxygen demand	2 milliliters sulfuric acid per liter	7 days
Dissolved oxygen, temperature, pH	Must be determined immediately at collection site	
Total solids	4 degrees Celsius	7 days
Volatile solids	4 degrees Celsius	7 days
Specific conductance	4 degrees Celsius	7 days

Analyses	Preservative	Maximum holding period
Alkalinity	4 degrees Celsius	24 hours
Acidity	4 degrees Celsius	24 hours
Heavy metals[1]	5 milliliters nitric acid per liter	6 months
Group I-II metals[2]	5 milliliters nitric acid per liter	6 months
Trace elements[3]	5 milliliters nitric acid per liter	6 months
Sulfate	4 degrees Celsius	7 days
Chloride	none	

[1]Lead, copper, iron, zinc, chromium and nickel
[2]Calcium, magnesium, potassium and sodium
[3]Selenium, boron, barium, molybdenum and arsenic

Summary

- Consult the laboratory before collecting and submitting a sample for analysis.
- Know which specific analyses are to be made on the sample.
- Collect representative samples.
- Avoid contaminating samples once they are collected.
- Immediately put samples on ice, or use the proper preservative.
- Refrigeration is the only preservation method to be used on samples taken for biological analysis.
- If there is doubt about the preservation method to use, store the sample on ice.
- Label all samples immediately and record them.
- List pertinent data on the label or accompanying letter.
- Keep the time interval between collection and analysis as short as possible.
