

QUALITY ASSURANCE

Quality assurance is a set of operating principles that, if strictly followed during sample collection and analyses, will produce data of known and defensible quality. The accuracy of analytical results can be stated with a high level of confidence (APHA, 1995). A quality assurance Plan in an analytical laboratory represents the following factors (USEPA, 1988):

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Quality assurance is composed of quality control and quality assessment.

A. Quality Control:

Quality control is a system designed to assure that the lab tests, reagents and instruments are operating properly. APHA (1995) states that a good quality control program consists of seven elements:

1. Certification of Operator Competency.
2. Recovery of Known Additions. Use the recovery of known additions as part of analyses protocols for 10% of samples by using the concentrated solutions so volume change in sample is negligible.
3. Analysis of Externally Supplied Standard. Whenever analyses of known additions does not result in acceptable recovery, analysis of externally supplied standards (certified reference materials) is necessary. Laboratory control standards are analyzed with concentrations between 5 and 50 times the MDL (Method detection level; the lowest reportable value) or near sample ambient levels, whichever is greatest.
4. Analyses of Reagent Blanks. Analyze a minimum of 5% of the sample load as reagent blank to monitor purity of reagents and the overall procedural blank.
5. Calibration with Standards. Measure at least three different dilutions of the standard when analysis is initiated. Verify the standard curve daily by analyzing one or more standards within the linear range, as specified in the individual method. Results are reported which are in the range of standard dilutions used.

6. Analysis of Duplicates. Analysis of duplicate sample is effective for assessing precision which is accomplished by analyzing 5% or more of the samples induplicate.
7. Control Charts. Three types of control charts are used in laboratories (Golden, 1984): a mean chart for standards - laboratory control standards or calibration check standard; a mean chart for background or reagent blank; and a range chart for replicate analyses. The procedural details can be found in APHA (1995).

B. Quality Assessment:

Quality Assessment is a set of procedures for determining the quality of data produced by a laboratory using internal and external quality control measures. Quality assessment allows feedback on how well the quality control program is working. Indicators of data quality include precision, accuracy, representativeness, comparability, and completeness, performance audits, and corrective actions.

Precision: Precision is a measure of the closeness with which repeated analyses of a given sample agree with each other. The relative standard deviation (RSD), also called the coefficient of variation, provides the overall precision of the study. The precision includes sampling error and errors in sample preparation and analyses. Duplicate analyses are performed for every 20th sample and RSD is calculated as

$$\text{RSD} = 100 \text{ S/M}$$

Where S = Standard deviation, and M = the mean. An RSD of less or equal to 10% is acceptable.

Bias: measure of systematic error (due to method or due laboratory's use of method). Best measured by a laboratory intercomparison study.

Accuracy: Accuracy is the degree of agreement between the measured and true value (Precision + Bias). The percentage recovery of known additions to a sample provides the measure of accuracy for the study. Every 20th sample, collected in sufficient quantity for splitting, should be spiked. The percent recover is calculated using the following formula:

$$\% \text{ Recovery} = 100 \text{ A}/(\text{B}+\text{C})$$

where

A = measured concentration of spiked sample
 B = measured concentration of unspiked sample
 C = concentration of known addition

An error of $\pm 10\%$ (a recovery of 90 to 110%) is acceptable. A corrective action is needed if the recovery is not within the acceptable limits.

Representativeness: It refers to how well the results represent the samples and how well the samples represent the population. It is assessed by investigating the variability among samples. For example, the required number of samples to develop a weekly composite sample may be calculated as:

$$n \geq t^2 S^2 / d^2$$

Where:

n = number of samples
 t = students 't' statistic for a given confidence level
 d = acceptable difference from the mean (± 20)
 S = sample standard deviation

Comparability: Certain data from the study can be compared to results obtained from other studies.

Completeness: It is measured as the percentage of total samples collected that were analyzed. Adequate amount of sample need to be collected to allow reanalysis of a sample if the sample is lost by accident or has a range beyond the standard curve. No more than 10% of samples should be missing in any analysis.

Performance Audits: The project should be subjected to a performance audit by submitting unknown samples to the laboratory quarterly. Reported results are compared to known values. The percentage recovery is calculated as

$$\text{Percent Recovery} = 100 (R-T)/T$$

Where:

R = reported value

T = true value

Performance with ± 25 is acceptable. Project supervisor makes unscheduled performance audits of all laboratory personnel to detect any violation from standard procedures and protocols using a checklist to document the manner in which a sample is treated from time of receipt to final reporting of the result.

Corrective Action: The project personnel should be capable of quickly identifying and correcting analytical problems. Sufficient volume of sample need to be collected to retest the sample which is failing to meet the quality control criteria.

Field Quality Assurance:

Field quality assurance represents the total integrated program for assuring the reliability of monitoring and measurement data. It consists of the calibration of field equipment, daily field logs, quality control samples, sample custody procedures, sample collection and preservation as discussed below.

1. Field Equipment:

Calibration and maintenance of field equipment is necessary to obtain reliable data for in -situ measurements such as temperature, pH, dissolved oxygen and samples for laboratory analysis. Dissolved oxygen meters and pH meters require daily or more frequent calibration. Stage recorders should be calibrated at every visit using a permanent outside staff gage. Precipitation gages are calibrated annually and checked weekly. Stage-discharge relationships should be developed by at least 15 discharge measurements using the velocity area method during the first year of the project. Subsequently the stage-discharge relationship should be checked with at least five ratings annually. A record should be maintained for all calibrations.

2. Field Logs: Field logs should be maintained for each field visit by each field worker. These logs should report name of field visitor, operating status of equipment, manual readings, and calibration checks. More often 1-page sheets are constructed relevant to a given project. Additional notes are recorded on personal log book.

3. Field Quality Control Samples: The four types of samples needed to assess field quality control (Burger 1987):

Field Duplicate: Two or more samples are collected simultaneously at a location to determine the variability associated with sample collection.

Trip Blank: Sample containers filled with distilled or deionized water are taken to the field and returned. This sample assesses contamination during transport and storage.

Sample Blank: This sample is obtained by passing deionized water through a nondedicated sampler, such as a portable pump. This blank is used to test contamination by a sampler.

Filtration Blank: Sample is collected by passing the deionized water through the field filtering apparatus to test the contamination by a filter and apparatus.

4. Sample Custody Procedures: Proper labeling of sample bottle is critical. Each sample should be dated and coded according to site, sample type, station number, and sample sequence. The actual sample container should be labeled with a number for identification. The sample number should be used in all laboratory books to identify the sample. It is a good practice to prelabel the sample containers before they are taken to the field. Transfer of samples from field

personnel to lab personnel is also recorded and records are maintained in the lab with the names and signature of persons leaving and receiving the custody.

5. Sample collection and Preservation: Different sampling procedures are followed depending upon the type of sample (grab or automatic) and type of water resource system (lake, stream or groundwater). A bottle used for grab sample is rinsed with sample water two to three times before filling unless the bottle contains preservative. The amount of sample depends upon the variables of interest. Suggested volumes are given in Table 1. However, the total volume of sample should also include the amount for a daily quality assurance program. Sometime the analysis of a sample may need to be repeated. It is generally recommended that volume should be doubled (Shelley, 1977).

Once a sample is collected, it may change its composition through physical, chemical and biological processes. So rapid analysis of samples are recommended (USEPA, 1983). However, rapid analysis of samples becomes difficult if the analytical labs are located at a greater distances away from sampling stations. In those situations, preservative techniques are used to slowing biological activity, hydrolysis, adsorption and volatility. The primary preservation methods are acidification, refrigeration, filtration, and preventing light from reaching the sample. Recommended methods of preservation, sample volume, type of sample container, and maximum holding time are summarized in Table 1. Transportation from field to the laboratory should be directed following some methods of preservation.

Table 1. Recommended method for sample collection and preservation (USEPA, 1983)

Measurements	Vol. Req. (ml)	Container P = plastic; G = glass	Preservative	Maximum holding time
Physical properties				
Color	50	P, G	Cool, 4 °C	48 hrs
Conductance	100	P, G	Cool, 4 °C	28 days
Hardness	100	P, G	HNO ₃ to pH < 2	6 mos
Odor	200	P, G	Cool, 4 °C	24 hrs
pH	25	P, G	None required	Analyze immediately
Residue				
Filterable	100	P, G	Cool, 4 °C	7 days
Nonfilterable	100	P, G	Cool, 4 °C	7 days
Total	100	P, G	Cool, 4 °C	7 days
Volatile	100	P, G	Cool, 4 °C	7 days
Settleable matter	1,000	P, G	Cool, 4 °C	18 hrs
Temperature	1,000	P, G	None required	Analyze immediately
Turbidity	100	P, G	Cool, 4 °C	48 hrs
Metals				
Dissolved	200	P, G	Filter on site HNO ₃ to pH < 2	6 mos
Suspended	200	P, G	Filter on site	6 mos
Total	100	P, G	HNO ₃ to pH < 2	6 mos
Chromium	200	P, G	Cool, 4 °C	24 hrs
Mercury dissolved	100	P, G	Filter	28 days
Total	100	P, G	HNO ₃ to pH < 2 HNO ₃ to pH < 2	28 days
Inorganics, nonmetallics				
Acidity	100	P, G	Cool, 4 °C	14 days
Alkalinity	100	P, G	Cool, 4 °C	14 days
Bromide	100	P, G	None required	28 days
Chloride	50	P, G	None required	28 days
Chlorine	200	P, G	None required	Analyze immediately
Cyanides	500	P, G	Cool, 4 °C NaOH to pH > 12 0.6g ascorbic acid	14 days
Fluoride	300	P, G	None required	28 days
Iodide	100	P, G	Cool, 4 °C	24 hrs
Nitrogen				
Ammonia	400	P, G	Cool, 4 °C H ₂ SO ₄ to pH < 2	28 days
Kjeldahl, total	500	P, G	Cool, 4 °C H ₂ SO ₄ to pH < 2	28 days
Nitrate plus Nitrite	100	P, G	Cool, 4 °C H ₂ SO ₄ to pH < 2	28 days
Nitrate	100	P, G	Cool, 4 °C	48 hrs
Nitrite	50	P, G	Cool, 4 °C	48 hrs
Measurements	Vol. Req. (ml)	Container P = plastic; G = glass	Preservative	Maximum holding time

Inorganics, nonmetallics (continued)

Dissolved oxygen				
Probe	300	G bottle and top	None required	Analyze immediately
Winkler	300	G bottle and top	Fix on site and store in dark	8 hrs
Phosphorous				
Ortho-phosphate dissolved	50	P,G	Filter on site Cool, 4 °C	48 hrs
Hydrolyzable	50	P,G	Cool, 4 °C	28 days
Total	50	P,G	H ₂ SO ₄ to pH <2 Cool, 4 °C	28 days
Total dissolved	50	P,G	H ₂ SO ₄ to pH <2 Filter on site Cool, 4 °C	24 hrs
silica	50	P only	Cool, 4 °C	28 days
sulfate	50	P,G	Cool, 4 °C	28 days
sulfide	500	P,G	Cool, 4 °C	7 days
			add 2 mL zinc acetate plus NaOH to pH > 9	
sulfite	50	P,G	None required	Analyze immediately
Organics				
BOD	1,000	P,G	Cool, 4 °C	18 hrs
COD	50	P,G	Cool, 4 °C	28 days
Organic carbon	25	P,G	H ₂ SO ₄ to pH <2 Cool, 4 °C	28 days
Phenolics	500	G only	H ₂ SO ₄ to pH <2 Cool, 4 °C	28 days

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