ASME PTC 19.11-2008

(Revision of ASME PTC 19.11-1997)

Steam and Water Sampling, Conditioning, and Analysis in the Power Cycle

Performance Test Codes

AN AMERICAN NATIONAL STANDARD

The American Society of Mechanical Engineers

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ASME
SETTING THE STANDARD

Date of Issuance: August 6, 2008

This Code will be revised when the Society approves the issuance of a new edition. There will be no addenda issued to this edition.

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CONTENTS

iii

NOTICE

All Performance Test Codes must adhere to the requirements of ASME PTC 1, General Instructions. The following information is based on that document and included here for emphasis and the convenience of the user of this Code. It is expected that the Code user is fully cognizant of Sections 1 and 3 of ASME PTC 1 and has read them prior to applying this Code.

ASME Performance Test Codes provide test procedures that yield results of the highest level of accuracy consistent with the best engineering knowledge and practice currently available. They were developed by balanced committees representing all concerned interests and specify procedures, instrumentation, equipment-operating requirements, calculation methods, and uncertainty analysis.

When tests are run in accordance with a code, the test results themselves, without adjustment for uncertainty, yield the best available indication of the actual performance of the tested equipment. ASME Performance Test Codes do not specify means to compare those results with contractual guarantees. Therefore, it is recommended that the parties to a commercial test agree before starting the test and preferably before signing the contract on the method to be used for comparing the test results with the contractual guarantees. It is beyond the scope of any Code to determine or interpret how such comparisons shall be made.

FOREWORD

The scope of Technical Committee No. 19 was to prepare Instruments and Apparatus Supplements describing the various types of instruments and methods of measurement likely to be prescribed in the ASME Performance Test Codes. Supplement Part 11, Water and Steam in the Power Cycle, presents the limits of application, treatment of interference, detailed procedure, and probable precision for selected methods of tests for determining steam purity and quality and condenser leakage.

The methods of measurement and prescribed instruments, including instructions for their use, are mandatory only when specified in the individual test codes. Other methods and instruments, even though included in the Instruments and Apparatus Supplement, shall not be used for formal performance tests unless all the parties agree.

Some of the instrumentation is associated in footnotes with one or more suppliers, especially in the adapted ASTM methods of test. In each instance, the reference provides information of special significance or value to the user of the document. Such citations in this and other Parts of the Performance Test Codes I and A Supplement are not to be construed as endorsements by the Society of a particular supplier's product.

Part of the material on Purity and Quality of Steam was printed in preliminary form in the June 1930 issue of *Mechanical Engineering*. A more formal draft of the first Part 11 was approved by the Standing Committee October 6, 1930 and approved and adopted by the Council of the Society on November 28, 1930. The first Part 21 on Leak Detection and Measurement was published in 1942 after similar approvals.

An updated revision of Part 11 was approved by the then Power Test Codes Committee on February 4, 1958 and approved and adopted by the Council of the Society by action of the Board on Codes and Standards on November 28, 1958. An updated revision of Part 21 was approved by the then Power Test Codes Committee on March 28, 1963 and approved and adopted by the Council of the Society by the action of the Board on Codes and Standards on February 14, 1964.

In June 1964, the PTC Committee No. 19, Part 11, was reorganized and instructed to update and rewrite the Supplement Parts on testing water and steam. The result was Supplement Part II, Water and Steam in the Power Cycle (Purity and Quality, Leak Detection and Measurement), superseding Parts 11 (1959) and 21 (1965). It was approved by the Performance Test Codes Committee on June 6, 1969 and approved and adopted by the Council of the Society by action of the Board on Codes and Standards on November 5, 1969.

The Code issued in 1997 was a revised and updated version of ASME/ANSI PTC 19.11-1970, Water and Steam in the Power Cycle (Purity and Quality, Leak Detection, and Measurement). It differed from its predecessor in a number of ways, including format and content. The format had been reorganized to follow the flow of the sample. The content had been expanded to reflect advances made since 1970, in all related areas affecting accurate measurements. The 1997 version of PTC 19.11 was approved by the ASME Board on Performance Test Codes on May 28, 1996 and adopted by the American National Standards Institute (ANSI) as an American National Standard on February 13, 1997.

Experience shows that the design, construction, and operation of sampling systems for thermal power plants have often been less than ideal. Such practices as withdrawing samples from drilled holes through the pipe or tube wall and sampling lines as large as $\frac{3}{4}$-in. pipe with numerous threaded fittings have been all too common. Ignoring the importance of maintaining proper fluid velocities in sampling lines has led to deposition of impurities on sample line surfaces so that the sample being analyzed bears little resemblance to the sample at its source. Improper sample conditioning (sample condensing and/or cooling and sample flow regulation) along with poor sampling locations and analysis methods have also taken their toll. And, finally, failure to permanently record and analyze the data taken can lead to expensive failures. The purpose of this Code is to present information on proper design, construction, and operation of steam and water sampling systems in the power cycle. The following sections are included:

(a) Section 1, Object, Scope, and Application, describes the aims, content, and limits of this Code.

(b) Section 2, Sample Selection Criteria, describes the components of a thermal power plant and what sample locations might be selected.

(c) Section 3, Obtaining the Sample, describes equipment design and operation for taking samples of saturated steam, superheated steam, and water.

(d) Section 4, Transporting the Sample, deals with proper sampling line design and operation. A table of satisfactory sample line sizes for various pressures and line lengths is presented.

(e) Section 5, Sample Conditioning, describes the recommended design and operation so as to provide proper sample flow, pressure, and temperature control, which is required for manual or automatic analysis.

(f) Section 6, Sample Analysis and Instrumentation, describes analyses that are usually made of samples. Principles of operation, precision, and literature references for analysis methods are also given.

(g) Section 7, Data Collection, Analysis, and Control, describes automatic instrumentation for collecting and storing data, means for retrieving and analyzing stored data (e.g., short- and long-term trends), and automated control purposes.

(h) Nonmandatory Appendices
(1) Nonmandatory Appendix A, Leakage Detection and Measurement
(2) Nonmandatory Appendix B, Throttling Calorimeter

This revision adds information on new sampling methods and instrumentation related to combined cycle plants using Heat Recovery Steam Generators (HRSG), new analytical instruments that aid in sample analysis, and other updates and advances in sampling methods and concepts developed since the last revision.

This edition was approved by the Board on Standardization and Testing on December 10, 2007 and by the ANSI Board of Standards Review as an American National Standard on January 15, 2008.

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Performance Test Codes

(The following is the roster of the Committee at the time of approval of this Standard.)

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viii

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General. ASME Codes are developed and maintained with the intent to represent the consensus of concerned interests. As such, users of this Code may interact with the Committee by requesting interpretations, proposing revisions, and attending Committee meetings. Correspondence should be addressed to

> Secretary, PTC 19.11 Committee
> The American Society of Mechanical Engineers
> Three Park Avenue
> New York, NY 10016-5990

Proposing Revisions. Revisions are made periodically to the Code to incorporate changes that appear necessary or desirable, as demonstrated by the experience gained from the application of the Code. Approved revisions will be published periodically.

The Committee welcomes proposals for revisions to this Code. Such proposals should be as specific as possible, citing the paragraph number(s), the proposed wording, and a detailed description of the reasons for the proposal, including any pertinent documentation.

Proposing a Case. Cases may be issued for the purpose of providing alternative rules when justified, to permit early implementation of an approved revision when the need is urgent, or to provide rules not covered by existing provisions. Cases are effective immediately upon ASME approval and shall be posted on the ASME Committee Web page.

Requests for Cases shall provide a Statement of Need and Background Information. The request should identify the Code, the paragraph, figure or table number(s), and be written as a Question and Reply in the same format as existing Cases. Requests for Cases should also indicate the applicable edition(s) of the Code to which the proposed Case applies.

Interpretations. Upon request, the PTC 19.11 Committee will render an interpretation of any requirement of the Code. Interpretations can only be rendered in response to a written request sent to the Secretary of the PTC 19.11 Committee.

The request for interpretation should be clear and unambiguous. It is further recommended that the inquirer submit his/her request in the following format:

Subject: Cite the applicable paragraph number(s) and the topic of the inquiry.

Edition: Cite the applicable edition of the Code for which the interpretation is being requested.

Question: Phrase the question as a request for an interpretation of a specific requirement suitable for general understanding and use, not as a request for an approval of a proprietary design or situation. The inquirer may also include any plans or drawings that are necessary to explain the question; however, they should not contain proprietary names or information.

Requests that are not in this format will be rewritten in this format by the Committee prior to being answered, which may inadvertently change the intent of the original request.

ASME procedures provide for reconsideration of any interpretation when or if additional information that might affect an interpretation is available. Further, persons aggrieved by an interpretation may appeal to the cognizant ASME Committee or Subcommittee. ASME does not "approve," "certify," "rate," or "endorse" any item, construction, proprietary device, or activity.

Attending Committee Meetings. The PTC 19.11 Committee regularly holds meetings, which are open to the public. Persons wishing to attend any meeting should contact the Secretary of the PTC 19.11 Committee.

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STEAM AND WATER SAMPLING, CONDITIONING, AND ANALYSIS IN THE POWER CYCLE

Section 1
Object, Scope, and Application

1-1 OBJECT

The object of this Code is to specify and discuss the methods and instrumentation for testing boiler make-up and feedwater, steam, and condensate in relation to performance testing as may be required in Performance Test Codes in one-time acceptance testing and continuous performance monitoring.

This Code also provides guidance to power-plant management, engineers, chemists, and operators in the design and operation of sampling systems for monitoring of cycle chemistry. The methods and equipment recommended herein may be useful for monitoring other influent and effluent streams of the power plant.

Contamination of the steam and water cycle must be at or less than the maximum specified for the performance test before a turbine, condenser, or deaerator performance test is made.

1-2 SCOPE

This Code includes
(a) sample selection
(b) sample collection and conditioning
(c) sample analysis
(d) data analysis

1-3 APPLICATION

The procedures, methods, and component information described in this Code are provided for guidance in obtaining, transporting, conditioning, and analyzing samples and detecting leaks in steam power cycles. A brief discussion of water treatment schemes is included but should not be interpreted as a recommendation of any particular method(s) or procedure(s). Application of these techniques should help ensure the performance determination (testing and operation) of significant components and of the steam cycle system in general.

Additional sampling points and/or analysis, redundancy, etc., are considerations for specific steam cycles but do not degrade the fundamental techniques detailed in the Code. This Code is applicable to any thermal power plant that involves water as a working fluid including, but not limited to, the following steam power cycles:
(a) fossil (utility/industrial base load and cycling)
  (1) combined cycle
  (2) bottoming cycle
  (3) topping cycle
  (4) utility nuclear[1]
  (5) solar
(b) specific areas not covered include the following:
  (1) makeup water treatment plant
  (2) service water cycle
  (3) cooling tower cycle
  (4) geothermal
  (5) techniques specific to handling radioactive fluids

1-4 UNCERTAINTY

Measurement uncertainty is not applicable to this Code. As stated in the object, this Code primarily provides guidance in the design and operation of sampling systems for monitoring cycle steam and water chemistry. Section 6 is included to provide a general overview of the analytical methods typically used in steam cycle water chemistry. Published analytical methods noted should be consulted for parameter uncertainty determination. Other noted analytical methodology should have parameter uncertainty determined and agreed to by the relevant parties prior to its acceptance for use in performance testing.

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[1] The handling and disposal of radioactive water and other hazardous materials require procedures beyond the scope of this Code. It is the user's responsibility to determine and comply with all applicable codes and regulations.

Section 2
Sample Point and Analysis Selection Criteria

2-1 INTRODUCTION

Sample point and analysis selection depend upon the purpose of testing. Each cycle component has a particular function. An agreement between the buyer and seller defines the specification. The sampling and analysis are designed to determine that the component is functioning as specified and that it is functioning properly in operation. Proper function is determined completely in a performance test by analyzing the sample to ascertain that all specifications are met. In operation, the proper function is assessed by less complete testing that concentrates on the most important impurities and most likely failures.

Section 2 focuses on the selection of sample point locations and the analyses that are commonly conducted for those locations. Most of the sample points are concerned with water quality assurance and equipment performance evaluation. For these points, continuous analysis is preferred. A few points are present largely to provide special data for analysis of problems. Grab samples will usually suffice at these points. Section 6 focuses on the analyses, their meaning, and the methods.

2-2 THERMAL POWER GENERATION CYCLES

The following discussion reviews components of a thermal power cycle that can affect the chemistry of the water and steam. Figure 2-2-1 shows these components and sampling points schematically for a generalized fossil cycle. The steam cycle of nuclear power plants is similar to the fossil plants except that many nuclear plants do not have a deaerating feedwater heater, and most nuclear plants have a moisture separator reheater that extracts moisture from the steam and superheats the vapor. Not all these components will necessarily be present in a particular application. Their presence in Fig. 2-2-1 does not imply that they are always needed.

Figure 2-2-2 shows a typical heat recovery steam generator (HRSG) system. There are many variations on the system, but the one shown has most of the features of an HRSG system. Three important variations are one or two pressure stages instead of three, the deaerating LP drum, and the once-through stages. In some systems, only two pressure stages exist. These systems are often nonreheat. In many systems, suction for a boiler feedpump is taken from the LP drum. This configuration makes the liquid withdrawal from the LP stage approximately 90% of the feedwater. The LP drum acts as a deaerator. In some systems, the HP or additional stages are once-through boiler technology. In these cases, no drum is present, although some steam separation equipment is usually present and used at startup.

There are systems where IP steam is used to cool combustion turbine parts. The steam purity requirements for the combustion turbine cooling may be significantly different from those for steam turbine. In those cases, the monitoring must support both sets of steam purity requirements.

Table 2-2 summarizes the sample points and analyses for both Figs. 2-2-1 and 2-2-2. The text and Table 2-2 suggest more analyses than most plants would use. They should be used as a guide for consideration of analyses at each location.

IMPORTANT NOTE: For proper testing, a sample must be provided at each cycle point for which there is a specification. Figures for other fossil cycles can be found in Chapter 17 of the ASME Handbook on Water Technology for Thermal Power Systems. [1]

Since nuclear power generation cycles can be vendor specific, more detailed information on them should be provided by vendors and/or other industry sources. However, the following general comments are appropriate:

(a) Special problems associated with radioactivity and gas concentrations in water are not addressed here.

(b) In BWR systems, no pH control additives are present; therefore, specific conductivity is the only conductivity measurement used. Oxygen, chloride, and sulfate are the only other common analyses. When zinc is added to the reactor to control radiation, a zinc analysis will be performed.

In systems with copper alloys in the condenser or feedwater heaters, the analysis of copper will commonly be appropriate. In all-ferrous systems, the analysis of copper will usually not be appropriate, but occasional analysis may be desired to be sure that no copper is entering the system from unsuspected sources.

2-3 WATER TREATMENT SCHEMES

The water treatment scheme also affects the sampling system and analyses performed at each location. Units on all volatile treatment (AVT) will not require phosphate analysis of the boiler water. However, if solid treatment (phosphate or caustic) of drum type units under emergency conditions is planned, the appropriate sampling and analysis equipment will be necessary. The amine selected for pH control may require special analytical techniques. Units on AVT(R), formerly called simply

Fig. 2-2-1 Generalized Fossil Cycle
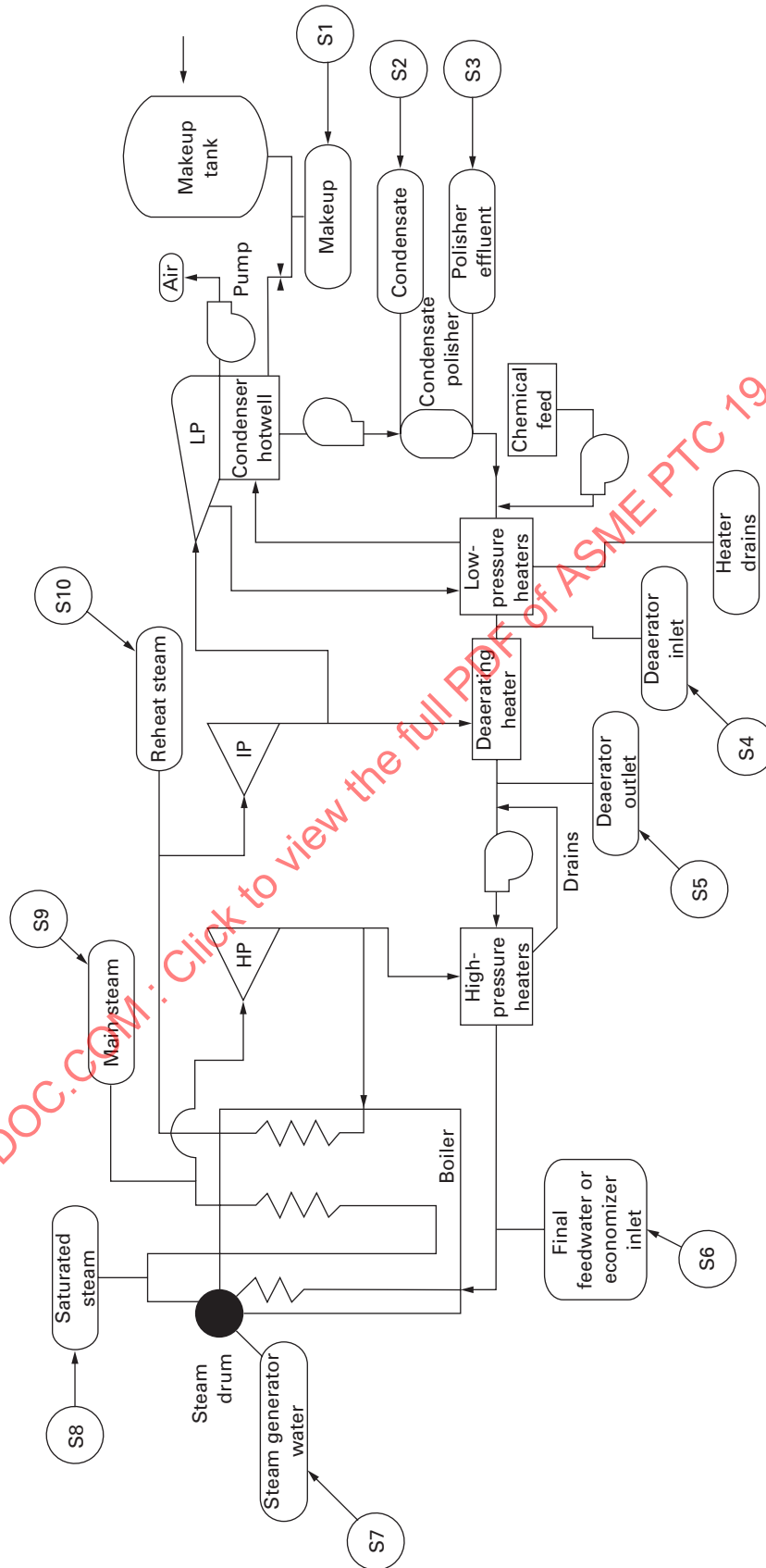
Fig. 2-2-2 Heat Recovery Steam Generator System
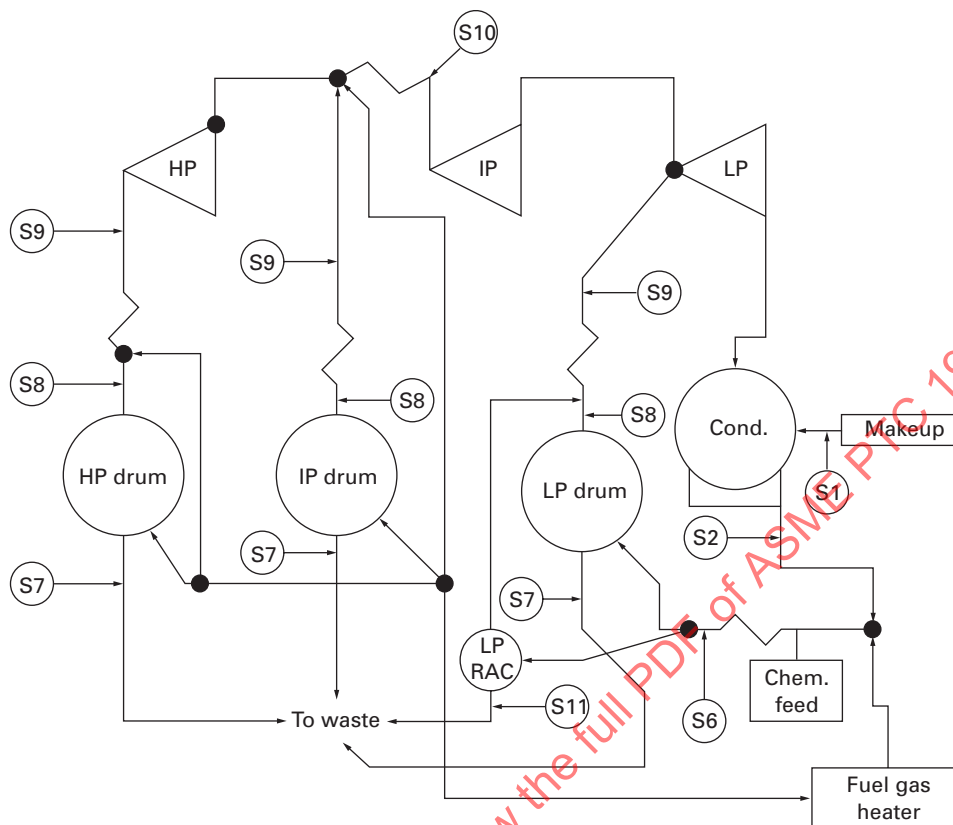
AVT, use a volatile pH control agent, usually ammonia, and an oxygen scavenger/reducing agent, such as hydrazine. The electrochemical potential is reducing.

For oxygenated water treatment (OT) schemes, the deaerating heater may be absent or not used. The selection of sampling depends on the way the deaerator is operated. Monitors for oxygen scavenger/reducing agent (such as hydrazine) are not used for OT or when AVT(O) is practiced. For OT schemes in recirculating boilers, a sample must be taken from a location, like the downcomer or waterwall header, and analyzed for oxygen to confirm that oxygen has been removed. [3]

AVT(O) is related to oxygenated treatment (OT) in that the electrochemical potential is oxidizing. It is generally achieved by controlling pH and allowing oxygen to reach an equilibrium defined by the equipment. No oxygen scavenger/reducing agent is dosed. Typical oxygen concentrations are in the 7 ppb to 25 ppb range.

2-4   MAKEUP

For this Code, the makeup is treated as the start of the system. The makeup is commonly stored in a tank vented to the atmosphere or in a tank where carbon dioxide and oxygen are controlled. The characteristics of the raw water will determine the design details of

the makeup train and the sampling and analysis required. Each makeup train effluent is sampled and will commonly be analyzed for specific conductivity, silica, and sodium. Other less common analyses will be for cation conductivity, pH, oxygen, total organic carbon (TOC), and hardness. The same analyses apply to makeup and condensate storage tanks.

2-5   CONDENSATE

The condenser usually has two functions. The first function is to condense steam and cool the condensate. To determine that the condenser is not leaking, the condensate pump outlet is commonly sampled for cation conductivity and sodium (water-cooled condenser designs). Other common analyses are specific conductivity, pH and silica (on line or grab sample), and metals (grab sample only), especially on air-cooled condensers. The second function is to remove volatile impurities, such as air, from the condensate. Air ejector flow rate and condensate oxygen are evaluated to confirm that this function is successful. Cation conductivity and degassed cation conductivity may also be used to confirm removal of volatile components.

Since the condenser is under vacuum, the condensate sample is usually collected from the condensate pump

4

Table 2-2 Sample Points and Analyses Location

Analysis	S1 Makeup	S2 Condensate	S3 Pol. Eff.	S4 DA In	S5 DA Out	S6 Final Feedwater	S7 SG Water [Note (1)]	S8 Saturated Steam	S9 & S10 Superheated Steam
Specific conductivity	N	L	N	...	...	N	N	...	...
Cation conductivity	R	N	N	N	...	...	L/N [Note (2)]	...	N
Degassed cation conductivity	...	R	...	...	...	...	...	...	R
pH	...	L	...	...	N	N	R	...	...
Sodium	L	L	N	...	...	N	L/N [Note (2)]	L	N
Silica	N	L	N	...	N	N	L	L	...
Oxygen	N	N	...	L	N	N	L [Note (2)]	L	...
Reducing agent (oxygen scavenger)	...	...	...	...	...	N	L/N [Note (2)]	...	...
Oxidation reduction potential (ORP)	...	...	...	N	...	R	...	...	...
Iron	...	L	L	...	...	N	S [Note (3)]	L	R
Copper [Note (2)]	...	L	L	...	...	N	S	L	R
Total organic carbon	L	...	...	...	...	L	L	...	...
Hardness	L	...	...	...	...	...	L [Note (2)]	...	...
Ammonia/amine	...	...	...	...	N	N	L [Note (2)]	...	...
Chloride	...	...	L	...	...	L	L	L	L
Sulfate	...	...	L	...	...	L	L	L	L
Phosphate	...	...	...	...	...	...	N [Note (2)]	...	...
Free alkalinity	...	...	...	...	...	...	N [Note (2)]	...	...

L = less common
N = normal
R = rare or occasional
S = less common except at startup

GENERAL NOTE: Moisture separator reheater, rotor air cooler (RAC), and feedwater drains are omitted from the table. See text.

NOTES:
(1) See text for BWR reactor water sampling and OT sampling.
(2) Water treatment or materials dependent.
(3) LP HRSG water should be tested routinely.

discharge. Air leaking into this pump can be confused with failure of the condenser to remove air. In water cooled condenser designs, additional sample points with independent sample pumps may be supplied for individual condenser sections to assist in the location of a leak. These individual hotwell samples are commonly analyzed for specific conductivity, cation conductivity, or sodium. Troughs at the bottom of condenser tube sheets may have in-situ conductivity probes.

2-6 POLISHER EFFLUENT

Condensate polishers are present in some cycles to remove trace impurities from the condensate and allow orderly shutdown in the event of a condenser leak. Their effluent is commonly sampled for specific conductivity, cation conductivity, sodium, and silica. These analyses should be made with online instruments. Chloride and sulfate analyses are becoming increasingly common. Copper and iron may also be analyzed.

2-7 DEAERATOR INLET

The deaerator inlet is commonly sampled for oxygen. Sampling may not be routine, but when problems develop with deaerator function, it is essential to know how much oxygen is entering the deaerator. See subsection 2-3 for OT comments. If Oxidation Reduction Potential (ORP) analysis is used, this is the preferred sampling location.

2-8 DEAERATOR OUTLET

The deaerator outlet (feed pump inlet) is commonly sampled for oxygen. When problems develop with the deaerator it is essential to know how much oxygen is leaving the deaerator. The deaerator outlet sample is usually downstream of the deaerator storage tank, where reaction between a reducing agent (oxygen scavenger) and oxygen may occur. The change in oxygen between the deaerator inlet and outlet indicates the effectiveness of the combination of mechanical deaeration and reducing agent.

2-9 FINAL FEEDWATER OR ECONOMIZER INLET

Since the feedwater pump can entrain oxygen, the final feedwater is the preferred location for determining compliance with the steam generator feedwater purity

5

requirements and is commonly used for dissolved oxygen control. The final feedwater or economizer inlet is commonly sampled for most of the impurities relevant to the steam cycle. The analyses usually include specific conductivity, cation conductivity, pH, ammonia or amines, sodium, silica, oxygen, reducing agent, copper (if appropriate), and iron. Less common analyses are chloride, sulfate, and Total Organic Carbon (TOC).

2-10 STEAM GENERATOR WATER

Steam generator is used in its most general sense here. It includes fossil-fired boilers, the secondary side of nuclear steam generators, Heat Recovery Steam Generators (HRSGs), and other steam generators as may be appropriate. Radioactive samples, such as PWR primary water and post-accident samples, are not included. BWR reactor water is essentially a steam generator sample and is included, but the special considerations due to its radioactivity are not addressed. Steam generator water is in contact with heat transfer surfaces. Contaminants in this water affect the performance and reliability of the steam generator. In recirculating steam generators, the steam generator water is a concentrated sample that is usually easier to analyze than the high-purity feedwater. This sample point exists at the flash tank in some once-through fossil steam generators and HRSGs but is usually sampled only during startup.

2-10.1 Steam Generators on Solids Treatment

Steam generators on solids treatment will commonly be sampled for specific conductivity, pH, free alkalinity (alkalinity not associated with phosphate present), phosphate (if appropriate), silica, and sulfite or other reducing agent (if appropriate). Less common are cation conductivity, sodium, chloride, sulfate, TOC, ammonia or amines, and hardness (where appropriate). Suspended iron (and copper, if appropriate) is commonly determined during startup.

2-10.2 Steam Generators on AVT

Steam generators on AVT will commonly be sampled for specific conductivity, cation conductivity, pH, sodium, and silica. Less commonly sampled are ammonia or amines, chloride, sulfate, and TOC. Suspended iron (and copper, if appropriate) is commonly determined during startup.

2-10.3 Steam Generators on OT

Steam generators on OT will usually be sampled only if they are the recirculating type. On these steam generators, a downcomer will commonly be sampled for cation conductivity and oxygen. Less commonly sampled are sodium, chloride, sulfate, silica, pH, specific conductivity, and ammonia.

2-10.4 BWR Reactor Water

Reactor water is commonly sampled for specific conductivity, chloride, sulfate, zinc (if zinc injection is in use), oxygen, silica, radioisotopes, and electrochemical corrosion potential. [4]

2-11 SATURATED STEAM

Saturated steam is sampled to determine the quantity of moisture and chemical carryover from the boiler drum. It is commonly analyzed for sodium and silica. Performance testing is usually based on sodium for fossil systems or on radioisotope tracer analysis for nuclear systems. In recirculating PWR systems, this sample point is the main steam, and cation conductivity is commonly analyzed. Less commonly analyzed are iron and copper (if appropriate), chloride, sulfate, and oxygen.

2-12 SUPERHEATED STEAM (INCLUDING REHEAT)

In fossil steam cycles with reheat, reheat steam is usually the preferred sample since it contains the effects of all attemperation water and any organic compounds that may have decomposed in the steam generator. Main steam shall be sampled when specified. Superheated steam is commonly analyzed for sodium and cation conductivity. Less common are degassed cation conductivity, pH, oxygen, silica, chloride, sulfate, and TOC. The superheated steam may occasionally be analyzed for iron and copper.

2-13 FEEDWATER HEATER DRAINS

Feedwater heater drains do not usually have water chemistry specifications. Samples from them are useful in determining the sources of metal oxide contamination in the cycle. Continuous analysis is not required, but occasional grab samples can be useful.

2-14 MOISTURE SEPARATOR REHEATER DRAINS

Moisture separator reheater (MSR) drains in nuclear power plants do not usually have water chemistry specifications. However, the ability to monitor them for specific conductivity, cation conductivity, and sodium may be useful for diagnosis of cycle chemistry problems.

2-15 ROTOR AIR COOLERS

Rotor Air Coolers (RACs) are found in combustion turbine systems and used to remove heat from the compressed air to generate intermediate or low-pressure steam. Typically, one analyzes RAC water for pH and silica. Silica is monitored because it can be soluble at working temperature and precipitates at ambient temperature.

2-16 BIBLIOGRAPHY

The following sources were cited using numbered references throughout this Section:

[1] Grabowski, H. A. "Management of Cycle Chemistry," Ch. 17 in ASME Handbook on Water Technology for Thermal Power Systems. American Society of Mechanical Engineers, 1989.

[2] Silvestri, G. J. "Steam Cycles," Ch. 1 in ASME Handbook on Water Technology for Thermal Power Systems. American Society of Mechanical Engineers, 1989.

[3] Cycle Chemistry Guidelines for Fossil Plants; Oxygenated Treatment. EPRI TR-102285, 1994.

[4] BWR Water Chemistry Guidelines Revision Committee, BWR Water Chemistry Guidelines — 1993 Revision. EPRI TR-1021134, 1993.

Section 3
Obtaining the Sample

3-1 INTRODUCTION

Section 3 specifies the equipment and procedures required to extract samples of saturated steam, superheated steam, and water from the power cycle.

3-2 WATER SAMPLING

Water and condensate in power plant systems often contain particulate matter, especially particles of metal oxides. Therefore, a two-phase system, consisting of particles dispersed in water, results. However, the difference in densities of water and particles is less than that between steam and water droplets, and the viscosity of water is much greater than that of steam. Therefore, particles in water follow changes in flow direction much more readily than water droplets in steam. Consequently, isokinetic sampling is normally not required for water samples (see subsection 3-3). Stratification and settling of particulates may occur in horizontal lines with low velocities.

Colloidal particles of metal oxides form deposits on their containers. These deposits tend to sorb dissolved impurities from the water. Therefore, it is important to design sampling systems so that the buildup of metal oxide deposits is minimized. Section 4 shows that the optimum velocity is 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s). In this velocity range, deposition and erosion stabilize at a constant value after 30 days of operation. See Section 4 for further discussion of sample line deposition.

3-2.1 Sampling Nozzles

Sampling nozzles for liquid samples shall not sample from the bottom of a horizontal pipe. To eliminate settling resulting from low velocities, the preferable location is in a vertical pipe with downward flow. Typical nozzles for sampling water are shown in Fig. 3-2.1.

3-2.2 Boiler Water Sample

The boiler water sample is an important sample that is commonly used to assess the blowdown requirements for the boiler. Since it is essential that the sample be taken from the location of maximum impurity concentration, the boiler manufacturer and system designers should be consulted for correct placement.

3-3 ISOKINETIC SAMPLING

Isokinetic sampling requires that the velocity of the fluid entering the sampler port(s) is exactly the same as the velocity of the stream being sampled at the location of the sampler. The effects of nonisokinetic sampling are illustrated in Fig. 3-3. [1]

3-4 SATURATED STEAM

Because saturated steam is often a two-phase fluid, made up of steam and small droplets of water, isokinetic sampling should be used. Since steam velocities vary with boiler load, normally it is not practical to sample isokinetically throughout the load range. Normally, the load of interest is full load or a guaranteed overload. The sampling system should be designed to provide isokinetic sampling at this design load. When isokinetic sampling is required over a range of steam flow rates, the sampling system shall be designed to provide adequate sample flow and isokinetic conditions for both the least and maximum anticipated steam flow rates. Assuming adequate pressure drop is available to transport the sample (see Section 4), steam velocity in the sampled pipeline should be at the high end of piping design recommendations to:

(a) assist in designing the sample system to get a representative sample across the load range

(b) help ensure that the condensed water film on the inside of the sampled pipeline is mixed with the steam vapor as well as possible.

Steam sample accuracy is always optimized if the sample is condensed as close to the source as possible. [1–5]

3-4.1 Sampling Nozzles

Stratification of suspended solids in horizontal steam pipes can influence the composition of the steam samples. To minimize the effects of stratification, it is recommended that steam sampling nozzles be located in long vertical pipes. To ensure that all water droplets are carried in the flow stream, downward flow is preferred. To minimize flow disturbance, the nozzle should be located at least 35 pipe diameters downstream and 4 pipe diameters upstream of in-line flow disturbances (valves, pipe bends, etc.). Nozzles that must be located in a horizontal pipe should be near the top of the pipe. [1]

Sampling nozzles can be either single-port or multiport configuration as specified or recommended by the

Fig. 3-2.1   Typical Nozzles for Sampling Water
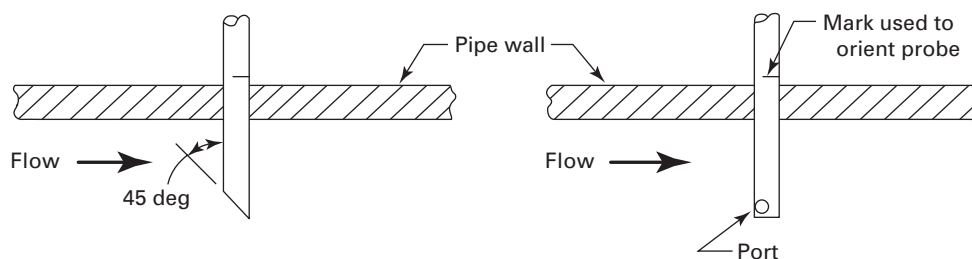
Fig. 3-3   Effects of Nonisokinetic Sampling
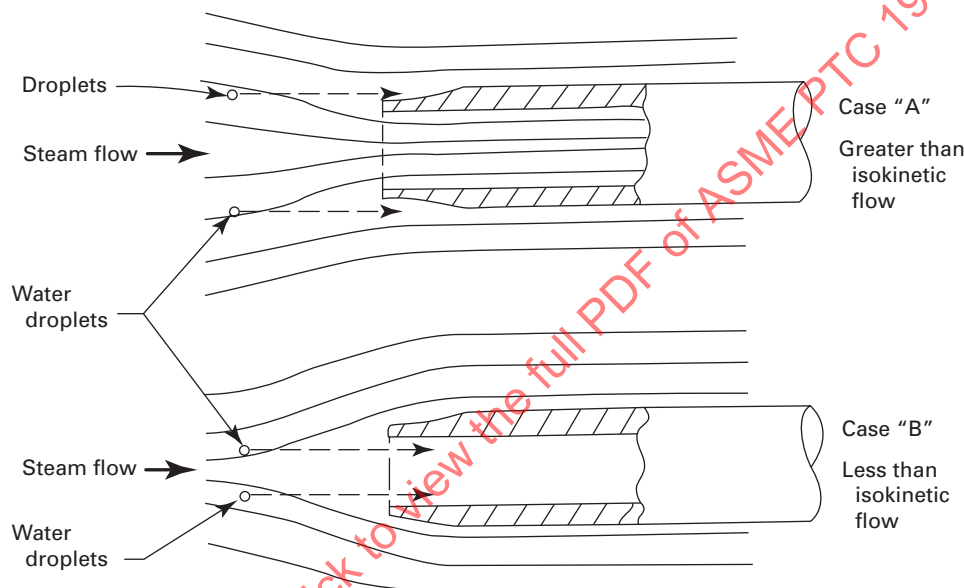
boiler manufacturer or design engineer. Sampling nozzles shall be adequately supported and designed to prevent failure due to flow-induced vibration, thermal stress cycling and other possible causes. Nozzles are most often made of AISI 316 or other austenitic stainless steel or alloy 600; however, the nozzle can be made of a material compatible with the sample pipeline material for weld compatibility. Weld joints used for dissimilar metals are subject to high thermal stresses due to different coefficients of thermal expansion. Care should be used in weld rod selection and inspection of all dissimilar metal weld joints.

A single port nozzle is used for valid steam sampling when it is positioned at a known distance from the inside of the steam pipe where a highly predictable velocity profile exists. Typically, this would be where fully developed turbulent flow is achieved enabling the determination of velocity at any location in the steam pipe. Single-port, off-center nozzles (Fig. 3-4.1) are most representative when they are located at a distance of approximately 0.2R of the pipe. This is the location where the actual and average velocities are equal. [1, 3] Reference [1]

Fig. 3-4.1   Typical Single-Port Nozzle

R = pipe radius
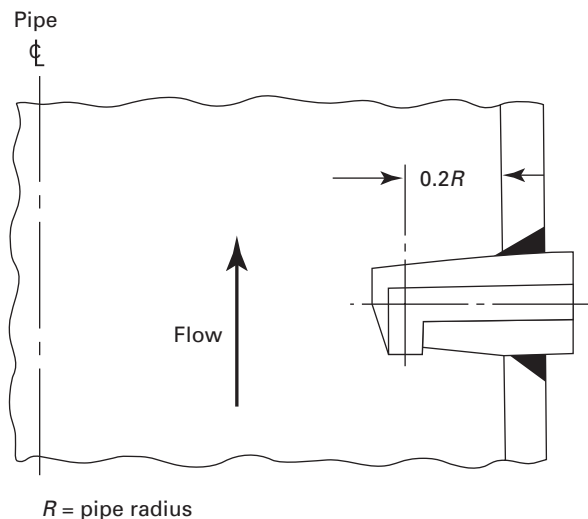
lists other single-port nozzle configurations. Multi-port nozzles that sample at various locations across the pipe cross section can also be used.

These nozzles should be used only at locations where the velocity profile across the pipe can be determined. Reference [1] details information on port location, port sizing, and internal passage sizing for multi-port nozzles. At least one boiler manufacturer equips most dry pans within the steam drum with a network of pipes for sampling saturated steam. [1]

Sample ports shall be drilled cleanly, using the standard drill size nearest to the calculated port diameter. The port inlet ends shall not be chamfered or rounded, and the outlet ends shall be free of burrs. The smallest recommended port diameter is $\frac{1}{8}$ in. (3.18 mm). Port diameters of less than $\frac{3}{32}$ in. (2.38 mm) are subject to plugging and shall not be used. Total port area shall be determined to maintain isokinetic sampling in the nozzle port(s) at the desired sampling rate and design steam flow. Appropriate design methods and validation should be followed to ensure the integrity of the nozzle fabrication and installation, as well as the ability to take an isokinetic sample.

3-5 SUPERHEATED STEAM

3-5.1 Introduction

Superheated steam is usually regarded as a single phase, which does not require isokinetic sampling. Most impurities in superheated steam are present in vaporous form and are thoroughly mixed with the steam vapor. However, superheater and reheater lines develop an oxide layer on the steam side, which continues to increase in thickness. High-pressure superheated steam has the ability to dissolve most contaminants. However, as steam pressure and temperature are reduced, many of the contaminants deposit on the inner surfaces of the nozzle and sample lines, causing biased analytical results. The physical properties of the oxide are different from the parent metal. Therefore, changing pressure and temperature cause the oxide layer to crack and exfoliate. [3] Because of this, using isokinetic sampling principles for superheated steam sampling allows for the collection and evaluation of these particles on cycle chemistry.

3-5.2 Sampling Nozzles

The nozzles described for use with saturated steam can also be used for superheated steam. Follow the recommendations in para. 3-4.1. In order to minimize the deposition of contaminants from superheated steam, several experts currently recommend injecting condensed and cooled sample directly into the superheated steam sampling nozzle. Due to concern for induced thermal stresses, few power plants have installed nozzles with integral condensate injection. Reference [1] includes a description of a superheated steam nozzle with condensate injection. Cooling the superheated steam sample as quickly as possible after obtaining it from the sampled pipeline is the only way to ensure a reasonably representative sample.

3-6 BIBLIOGRAPHY

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[4] Cobb, R.V., and Coulter, E.E. "The Prevention of Errors in Steam Purity Measurement Caused by Deposition of Impurities in Sampling Lines," Proceedings the American Society for Testing and Materials 61 (1961): 1386-1395.

[5] Lawlor, M., and Clark, C. "An Experimental Investigation of Some of the Factors Which Influence the Accuracy of Steam Sampling," ASME Publication 61-WA-266, September 8, 1961.

3-7 FURTHER READING

Berry, W. E., and Diegle, R. B. "Survey of Corrosion Generation, Transport, and Deposition in Light Water Reactors," EPRI NP-522, Final Report, March 1979.

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Section 4
Transporting the Sample

4-1 INTRODUCTION

Transporting the sample consists of conveying the sample from the sampling nozzle, where the sample is collected, to the location where sample conditioning (see Section 5) is accomplished. Samples flowing through sample lines can be affected in many ways; the longer the sample line, the more likely the sample is to be affected. Impurities in the sample stream may be affected by physical phenomena, such as deposition and erosion; thermodynamic changes, such as throttling and heat loss; and chemical and physical changes, such as reactions of oxygen scavengers, crystallization, and sorption. The purpose of Section 4 is to identify such changes and indicate how these changes can be minimized.

Almost any fluid flowing through a tube or stored in a container will leave or pick up some residue. All samples experience pressure drop as they flow through the sample line. Hot samples also have significant temperature changes resulting from heat loss from the tube surface.

This Section discusses transport of samples of superheated steam, saturated steam, and liquids, including condensate and boiler water. Most often, the superheated samples will lose the superheat within the sample tube. Frequently, saturated and superheated steam samples will fully condense within the sample tube. Design recommendations for liquid samples should then be applied to these condensed samples.

4-2 SAMPLE LINE CONSTRUCTION

The Power Piping Code, ASME B31.1 [1], applies to tubing outside the boiler setting but does not address tubing as small as is normally used for sample lines. The use of small tubing does not violate the code; the code simply does not address the use of small tubing. Therefore, the designer is responsible for the sample line design. Reference [2] is a source of information for the design of small tubing systems.

4-2.1 Valves

Safety requirements and most construction codes require the use of root valves at the sample source. Safety considerations may also require double valves for high-pressure applications. Valves selected for root-valve service are likely to be larger and installed with heavier piping than the rest of the sampling line. This can result in deposition and release of material that will produce periodic bursts of particulate. Root valves should be

selected with minimum bore diameters that will allow the sample velocity to approach 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s), which is recommended for other parts of the sample line.

Additional valves between the root valve(s) and sample conditioning system are not recommended. When additional valves must be installed, they should be selected to minimize flow disruptions and maintain flow velocities.

4-2.2 Material Selection and Preparation

The wall thickness and material shall be suitable for the temperature and pressure of the sample source and shall be of corrosion-resistant material. AISI 316 stainless steel is the preferred material that can be obtained in either seamless (ASME SA-213) or welded (ASME SA-249) construction. Reference [1] includes design formulas and allowable pressure-temperature rating data for stainless steel tubing with additional data available in Ref. [2]. Tubing inside diameters should be selected based upon sample velocities and pressure drops as discussed in this Section. All fittings should be selected based upon their temperature and pressure ratings and be made of materials compatible with the sample lines and sample.

4-2.3 Installation

Sample lines shall be free of dead legs, particulate traps (such as strainers), and low velocity zones. Sample lines should be as short as practical. They shall be adequately supported to prevent fatigue failure from vibration but free to expand and contract with temperature changes. Normally, sample lines should not be insulated. Where contact of personnel with hot lines is possible, suitable protection or guards shall be provided. Sample tubing shall be protected from damage resulting from adjacent activities.

4-2.4 Fabrication

Welding of small diameter [$\frac{1}{4}$ in. (6 mm) to $\frac{3}{8}$ in. (10 mm) outside diameter] can result in burn-through with a significant reduction in the original bore. Care should be employed to minimize the shrinkage in all welded joints. Compression fittings from several reliable manufacturers can also be used. Tubing bends are recommended instead of right-angle fittings. Right-angle fittings have sharp changes in direction that result in high pressure drop and have increased probability of

particle entrapment. Large-radius tube bends are preferred.

Hacksaws and tubing cutters cause burrs that can restrict sample flow and may cause plugging. Burrs shall be removed before fittings are applied. Lines should be blown out with clean, oil-free air or flushed prior to installation to remove metal filings and shavings resulting from removing burrs.

4-3 DEPOSITION

Virtually any fluid flowing through a tube or stored in a container will leave or pick up some residue. The loss or gain of contaminants at the tube wall can cause biased results from chemical analysis. There are a multitude of factors that contribute to deposition on the tube wall. The most prominent mechanisms include crystallization resulting from solubility changes, settling resulting from gravity and hydrodynamic forces, and electrostatic attraction of charged particles to the tube wall. Reference [3] discusses in detail a number of theories related to deposition on fluid boundaries.

Settling results when particles are transported to the vicinity of the wall by fluid eddies and across the boundary layer by their inertia, diffusion, or gravity. Some of the particles that reach the wall stick to the wall. A theoretical "sticking probability" is used to determine whether the particle will deposit on the wall. Some particles that stick are later eroded from the wall by the fluid drag force. The eroded particles become re-entrained in the fluid stream. Both the rate of deposition and the rate of erosion are velocity dependent. Steady-state deposit weights are at a minimum with liquid velocities at 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s). Minimum deposits are desirable because they reach equilibrium in a shorter period of time and are considered less susceptible to particulate bursts where an area of previously deposited material is swept into the stream.

The waters involved in power plant operation are stored in and transported through pipes and tubes of iron-bearing material. These waters contain various oxides of iron in colloidal form. The effluent from demineralizers may also contain colloidal particles of ion exchange resins. All colloidal material tends to form deposits as the fluid flows through pipes and tubes.

4-3.1 Sorption of Dissolved Species

Tube wall deposits are porous and tend to sorb appreciable amounts of dissolved species by ion exchange, absorption, adsorption, or other mechanisms. Therefore, when the deposit is disturbed by a change in velocity or other means, a particulate burst can occur that consists of not only deposit material but also dissolved species. These bursts can cause spikes in the output of analytical instruments and grab samples.

4-3.2 Crystallization

Most contaminants can be dissolved in superheated steam. However, as steam pressure and temperature are reduced, the solubility of many contaminants is decreased, and the contaminants are deposited on the inner surfaces of the containing tube. [4] This condition has been found to be prevalent only in regions of dry wall tube where the temperature of the tube wall exceeds the saturation temperature of the steam.

4-4 SATURATED STEAM

The preferred method to sample saturated steam is to condense the sample as near to the source as is possible, then size the condensate portion of the line to maintain the desired 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s) liquid velocity. Due to the lack of sufficient cooling water near the sample source, few plants currently use source cooling. The vast majority of power-generating stations cool their steam samples at a central sampling station, most frequently located in the chemistry laboratory. This practice has resulted in many sampling lines exceeding 400 ft (120 m) in length. The discussion that follows assumes that steam samples are cooled at an analysis panel that is remote from the sample source.

NOTE: It is strongly recommended that new and existing plants provide for source cooling of steam samples to maximize the ability to obtain a representative sample.

A saturated steam sample originates at the sampling nozzle as vapor with entrained liquid droplets. As flow proceeds down the tube, heat loss from the outside tube surface causes a liquid film to form on the inside surface of the tube. The liquid film moves down the tube at significantly slower velocity than the steam vapor. The surface of the liquid has moving waves that vary with the liquid and vapor velocities. If the steam velocity is sufficiently high, then droplets of liquid are entrained into the moving steam from the wave crests. Simultaneously, droplets carried by the steam flow impinge on the liquid film and become entrapped in it. The film thickness gradually increases with additional condensation. When the film reaches sufficient thickness, the flow develops to slug or churn flow where large bubbles of steam flow faster than the accompanying liquid and bypass the liquid between the bubbles. Gradually, the size of the bubbles decreases until all steam condenses, and single-phase liquid flow results. If the sample line is short, then all phases may not be encountered. [5] The term "condensing length" will be used to refer to the length of tube where the entire steam sample has condensed.

A second scenario can also occur with saturated steam samples. When the steam velocity entering the sample line is high, then pressure drop can alter the flow characteristics of the sample. High steam velocity is accompanied by high pressure drop. The high pressure drop

results in expansion of the steam that causes higher steam velocity with higher incremental pressure drop. This condition causes a compounding effect of both the velocity and local pressure drop. Depending upon the steam pressure, a saturated steam sample can deviate from the saturation curve and enter the superheat region. Steam samples are usually at pressures where these conditions do not exist. However, combined cycle plants with multiple pressure heat recovery steam generators typically produce steam at pressures less than 500 psig (3.45 MPa). These samples will experience extremely high pressure drop, which can be maintained only for shorter sample tube lengths [typically less than 200 ft (60 m)]. Longer sample lines will experience flow reductions, which result in loss of flow.

4-4.1 Deposition

Saturated steam is less likely to form deposits inside sample lines than either liquid or superheated samples. Saturated steam has a large specific volume compared with the condensed liquid. The large volume of steam results in high steam velocities in properly designed sample lines. The high velocity steam is accompanied by fast-moving liquid droplets that erode any deposits that tend to form.

Long sample lines can result in sufficient heat loss from the tube surface to condense the entire sample. This condition is most common at higher source pressures. Fully condensed samples and samples with low steam content have greatly reduced volume with accompanying lower velocities. Liquid sample velocities of less than 5 ft/sec (1.5 m/s) will promote deposition of particles that have the ability to sorb dissolved species. See subsection 4-3. Such conditions shall be minimized by proper selection of sample line dimensions.

4-4.2 Sample Flow Rate

A change in flow rate of a saturated steam sample will result in a change in velocity at the steam inlet proportional to the change in flow rate. However, it will also result in a change in the condensing length. The various regions of two-phase flow will then shift along the sample line. Areas of tubing that have liquid flow at one flow rate will experience two-phase flow at a higher flow rate. Calculations indicate that flow-rate changes of about 10% can cause velocity changes of a factor of two or three in regions near the fully condensed length. This region near the condensing length will experience "slug" flow with fluctuating velocities, which will tend to scrub the wall of previously deposited material. Similarly, flow decreases will result in reducing the condensing length with liquid flow occupying portions of tubing, which previously had "slug" or "bubbly" flow.

Therefore, constant sample-line flow should be maintained, or results should be interpreted accordingly.

4-4.3 Steam Sample Line Sizing

Sample lines for saturated steam can best be designed by using a computer program. The computer program can determine heat loss and pressure drop for any flow condition. It can then determine changes resulting from expansion or differing flow regimes. Tables 4-4.3-1 and 4-4.3-2 summarize a series of calculations performed to size steam-sample tubing for two ranges of steam pressure. Three relatively standard tube sizes were evaluated at nine separate pressures for three flow rates of saturated steam and for three flow rates of superheated steam at each pressure. All sample flow rates refer to cooled condensate at a temperature of 77°F (25°C).

NOTE: The values in Tables 4-4.3-1 and 4-4.3-2 are based upon tubing at the nominal inside diameter and are based upon straight tubing. A nominal amount of bends will be included in all sampling lines. If an unusual number of bends is used in any sampling line, allowance for the additional pressure drop should be made.

4-5 SUPERHEATED STEAM

4-5.1 Introduction

Superheated steam samples originate at the sample source as a single-phase fluid with dissolved contaminants. Several studies [4] have shown that super-heated steam samples deposit contaminants on the dry wall portion of the sample line where the tube wall temperature is above the saturation temperature of the steam. To minimize loss of contaminants, it is recommended that superheat be removed from steam samples as soon as possible.

NOTE: It is strongly recommended that new and existing plants provide for source cooling of steam samples to maximize the ability to obtain a representative sample.

Most superheated steam samples will lose all superheat soon after the sample leaves the sampling port. Subsequent to this, these samples behave in the same manner as saturated steam samples discussed previously. Within the superheated region, these samples have higher velocities than the saturated steam samples. Table 4-4.3-1 includes recommended sample line sizes for several sample flow rates at pressures from 500 psia (3.45 MPa) to 2,800 psia (19.3 MPa).

4-5.2 Recirculation System

One method to avoid deposition of contaminants on the dry tube wall is to inject a portion of the condensate from the superheated steam sample into the steam nozzle or as close to the nozzle as practical. As discussed in Section 3, water injection into the sampling nozzle is seldom used due to concern for high thermal stresses within the sampling nozzle.

Table 4-4.3-1 Recommended Sample Tube Sizes for Pressures ≥ 500 psia
(Used with permission — Sentry Equipment Co.)

Pressure, psia	Condition	Sample Flow, cc/min	$\frac{1}{4}$-in. O.D. × 0.049-in. Wall				$\frac{3}{8}$-in. O.D. × 0.065-in. Wall				$\frac{1}{2}$-in. O.D. × 0.083-in. Wall			
			Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec
2,800	Saturated	1,300	>700	190	39	7.1	>700	120	15	2.5	>700	90	8	1.3
	Saturated	1,000	>700	140	30	5.2	>700	90	12	1.9	>700	70	6	1.0
	Saturated	700	>700	90	21	3.4	>700	60	8	1.3	>700	50	4	0.7
	1,000°F	1,300	>700	600	100	*	>700	250	39	2.7	>700	190	21	1.4
	1,000°F	1,000	>700	310	78	5.6	>700	190	30	1.9	>700	150	16	1.0
	1,000°F	700	>700	200	55	3.5	>700	130	21	1.3	>700	100	11	0.7
2,400	Saturated	1,300	>700	310	53	7.4	>700	170	20	2.6	>700	130	11	1.3
	Saturated	1,000	>700	210	41	5.2	>700	130	16	1.9	>700	100	8	1.0
	Saturated	700	>700	140	29	3.5	>700	90	11	1.3	>700	70	6	0.7
	1,000°F	1,300	150	*	120	*	>700	300	47	2.7	>700	220	25	1.4
	1,000°F	1,000	>700	400	93	5.9	>700	220	36	2.0	>700	170	19	1.0
	1,000°F	700	>700	240	65	3.6	>700	160	25	1.3	>700	120	14	0.7
2,000	Satirated	1,300	250	*	87	*	>700	230	27	2.6	>700	170	15	1.3
	Saturated	1,000	>700	290	55	5.4	>700	170	21	1.9	>700	130	11	1.0
	Saturated	700	>700	180	38	3.5	>700	120	15	1.3	>700	90	8	0.7
	1,000°F	1,300	N.R.	. . .	150	. . .	>700	350	57	2.8	>700	260	31	1.4
	1,000°F	1,000	300	*	100	*	>700	260	44	2.0	>700	200	24	1.0
	1,000°F	700	>700	290	80	3.6	>700	180	31	1.3	>700	140	17	0.7
1,750	Saturated	1,300	150	*	140	*	>700	270	33	2.6	>700	200	18	1.4
	Saturated	1,000	>700	420	66	5.6	>700	200	25	1.9	>700	160	14	1.0
	Saturated	700	>700	220	46	3.5	>700	140	18	1.3	>700	110	10	0.7
	1,000°F	1,300	N.R.	. . .	170	. . .	>700	400	67	2.9	>700	290	36	1.4
	1,000°F	1,000	150	*	130	*	>700	300	51	2.0	>700	230	28	1.0
	1,000°F	700	>700	340	93	3.7	>700	200	36	1.3	>700	160	19	0.7
1,500	Saturated	1,300	N.R.	. . .	110	. . .	>700	320	40	2.7	>700	240	22	1.4
	Saturated	1,000	180	*	110	*	>700	240	31	2.0	>700	180	17	1.0
	Saturated	700	>700	270	56	3.6	>700	170	22	1.3	>700	130	12	0.7
	1,000°F	1,300	N.R.	. . .	200	. . .	>700	450	79	3.0	>700	330	42	1.4
	1,000°F	1,000	N.R.	. . .	160	. . .	>700	330	61	2.0	>700	250	33	1.0
	1,000°F	700	500	470	110	3.9	>700	230	42	1.3	>700	180	23	0.7
1,250	Saturated	1,300	N.R.	. . .	130	. . .	>700	390	50	2.8	>700	280	27	1.4
	Saturated	1,000	80	*	130	*	>700	280	39	2.0	>700	220	21	1.0
	Saturated	700	>700	390	70	3.7	>700	190	27	1.3	>700	150	15	0.7
	1,000°F	1,300	N.R.	. . .	250	. . .	>700	550	96	*	>700	380	51	1.5
	1,000°F	1,000	N.R.	. . .	190	. . .	>700	390	74	2.1	>700	290	40	1.0
	1,000°F	700	150	*	130	*	>700	260	51	1.3	>700	200	28	0.7
1,000	Saturated	1,300	N.R.	. . .	170	. . .	>700	500	65	3.0	>700	340	35	1.4
	Saturated	1,000	N.R.	. . .	130	. . .	>700	350	50	2.0	>700	260	27	1.0
	Saturated	700	N.R.	. . .	91	. . .	>700	230	35	1.3	>700	180	19	0.7
	1,000°F	1,300	N.R.	. . .	320	. . .	400	*	120	*	>700	440	65	1.5
	1,000°F	1,000	N.R.	. . .	240	. . .	>700	470	93	2.2	>700	330	50	1.1
	1,000°F	700	N.R.	. . .	170	. . .	>700	300	65	1.3	>700	230	35	0.7

14

Table 4-4.3-1 Recommended Sample Tube Sizes for Pressures ≥ 500 psia (Cont'd)
(Used with permission — Sentry Equipment Co.)

Pressure, psia	Condition	Sample Flow, cc/min	¼-in. O.D. × 0.049-in. Wall				⅜-in. O.D. × 0.065-in. Wall				½-in. O.D. × 0.083-in. Wall			
			Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec
750	Saturated	1,300	N.R.	...	**230**	...	150	*	**98**	*	>700	420	48	1.5
	Saturated	1,000	N.R.	...	**180**	...	>700	480	68	2.2	>700	320	37	1.0
	Saturated	700	N.R.	...	**130**	...	>700	290	48	1.3	>700	220	26	0.7
	1,000°F	1,300	N.R.	...	**420**	...	N.R.	...	**160**	...	>700	560	88	*
	1,000°F	1,000	N.R.	...	**330**	...	300	*	**130**	*	>700	400	68	1.1
	1,000°F	700	N.R.	...	**230**	...	>700	380	88	1.4	>700	280	47	0.7
500	Saturated	1,300	N.R.	...	**360**	...	N.R.	...	**140**	...	450	*	73	*
	Saturated	1,000	N.R.	...	**270**	...	N.R.	...	**100**	...	>700	420	56	1.1
	Saturated	700	N.R.	...	**190**	...	500	440	73	1.4	>700	280	39	0.7
	1,000°F	1,300	N.R.	...	**640**	...	N.R.	...	250	...	300	*	130	*
	1,000°F	1,000	N.R.	...	**500**	...	N.R.	...	**190**	...	>700	550	100	*
	1,000°F	700	N.R.	...	**350**	...	200	*	**130**	*	>700	350	72	0.7

GENERAL NOTE:

Cond. L = length where all steam has been condensed. An asterisk (*) in this column indicates that the steam was not fully condensed in the maximum recommended length.

Cond. V_{min} = velocity of the condensate at a 500 ft (154 m) length. Since the density of water varies with temperature, any sampling tube shorter than 500 ft (154 m) would have terminal velocities slightly higher than this value; longer tubes would have slower velocities. As above, an (*) in this column indicates that the steam is not fully condensed in the recommended length or has not condensed within 500 ft (154 m).

Max. L = maximum recommended length of tube for that pressure and flow rate. An "N.R." in this column indicates that this size of sample tube is not recommended for any length since the compounded pressure drop is excessive.

Steam V_{max} = maximum velocity of the steam in the recommended length. A boldface value in this column indicates that the steam velocity is increasing due to expansion. Boldface values are taken at the maximum recommended length. The required initial steam velocity is shown for all values where the tube size is not recommended for any length.

Experience with vaporous carryover of silica in saturated steam shows that if the silica in the steam is kept sufficiently low, no silica deposits on the turbine. [7] It has been suggested that if the concentrations of impurities in superheated steam are sufficiently low, objectionable deposits of impurities on sample lines will not occur. Because superheated steam contains several types of impurities and each impurity has its own solubility characteristics, the present state of the art is not sufficient to predict whether or not sample recirculation is necessary. Even though the superheated steam sample presents difficulties, efforts should be made to extract and transport the most representative sample possible.

If an accurate measurement is required to determine whether or not a turbine manufacturer's specification for steam purity is being met, then the validity of the steam sample must be established. Reference [4] includes a test that can be performed to determine whether a recirculation system is required.

4-6 LIQUID SAMPLES

Sample lines for liquid samples should be sized to maintain the sample velocity at 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s). This velocity range will result in deposit weight reaching equilibrium after approximately 30 days of stable operation. This range is considered optimum to reduce sample line deposits and provide samples with moderate time delay. Reference [3] shows the effects of various fluid velocities on equilibrium deposit weights and the time periods needed to establish equilibrium.

4-7 BIBLIOGRAPHY

The following sources were cited using numbered references throughout this Section:

[1] ASME B31.1,"Power Piping," 1995 ed. The American Society of Mechanical Engineers.

Table 4-4.3-2   Recommended Sample Tube Sizes for Pressures ≤ 400 psia
(Used with permission — Sentry Equipment Co.)

Pressure, psia	Condition	Sample Flow, cc/min	$\frac{3}{8}$-in. O.D. × 0.65 in. Wall				$\frac{1}{2}$-in. O.D. × 0.083 in. Wall				$\frac{5}{8}$-in. O.D. × 0.083 in. Wall			
			Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec
400	Saturated	900	100	*	**191**	*	>600	515	63	1.0	>600	380	33	0.5
	Saturated	700	200	*	**139**	*	>600	375	49	0.7	>600	295	26	0.4
	Saturated	500	>600	375	65	0.9	>600	260	35	0.5	>600	210	19	0.3
	1000°F	900	75	*	**239**	*	>600	*	115	*	>600	460	61	0.5
	1000°F	700	150	*	**167**	*	>600	455	89	0.7	>600	355	47	0.4
	1000°F	500	>600	495	118	1.0	>600	315	64	0.5	>600	255	34	0.3
350	Saturated	900	N.R.	*	**134**	*	>600	595	72	1.0	>600	415	38	0.5
	Saturated	700	100	*	**135**	*	>600	410	56	0.7	>600	315	30	0.4
	Saturated	500	>600	450	74	0.9	>600	280	40	0.5	>600	225	21	0.3
	1000°F	900	N.R.	*	**247**	*	500	*	132	*	>600	500	70	0.5
	1000°F	700	100	*	**175**	*	>600	505	102	0.7	>600	380	54	0.4
	1000°F	500	300	*	**112**	*	>600	335	73	0.5	>600	270	38	0.3

Pressure, psia	Condition	Sample Flow, cc/min	$\frac{1}{2}$-in. O.D. × 0.83 in. Wall				$\frac{5}{8}$-in. O.D. × 0.083 in. Wall				$\frac{3}{4}$-in. O.D. × 0.095 in. Wall			
			Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec
300	Saturated	900	400	*	**105**	*	>600	455	44	0.5	>600	375	30	0.3
	Saturated	700	>600	470	65	0.7	>600	345	35	0.4	>600	290	23	0.2
	Saturated	500	>600	310	47	0.5	>600	245	25	0.3	>600	210	17	0.2
	1000°F	900	275	*	**143**	*	>600	545	81	0.5	>600	450	54	0.3
	1000°F	700	>600	590	120	0.8	>600	415	63	0.4	>600	350	42	0.2
	1000°F	500	>600	370	85	0.5	>600	295	45	0.3	>600	250	30	0.2
250	Saturated	900	200	*	**158**	*	>600	510	53	0.5	>600	420	36	0.3
	Saturated	700	>600	*	**78**	*	>600	385	41	0.4	>600	325	28	0.2
	Saturated	500	>600	350	56	0.5	>600	270	30	0.3	>600	230	20	0.2
	1000°F	900	150	*	**164**	*	>600	*	98	*	>600	500	66	0.3
	1000°F	700	350	*	**113**	*	>600	460	76	0.4	>600	385	51	0.2
	1000°F	500	>600	420	102	0.5	>600	320	54	0.3	>600	275	36	0.2
200	Saturated	900	100	*	**191**	*	600	*	66	*	>600	475	44	0.3
	Saturated	700	175	*	**124**	*	>600	445	51	0.4	>600	365	34	0.2
	Saturated	500	>600	420	69	0.5	>600	310	37	0.3	>600	260	25	0.2
	1000°F	900	100	*	**246**	*	>600	*	123	*	>600	565	82	0.3
	1000°F	700	125	*	**136**	*	>600	525	95	0.4	>600	430	64	0.2
	1000°F	500	>600	525	128	0.5	>600	360	68	0.3	>600	305	45	0.2
150	Saturated	900	N.R.	*	**164**	*	400	*	103	*	>600	575	58	0.3
	Saturated	700	75	*	**176**	*	>600	550	67	0.4	>600	430	45	0.2
	Saturated	500	200	*	**106**	*	>600	360	48	0.3	>600	290	32	0.2
	1000°F	900	N.R.	*	**312**	*	300	*	134	*	>600	*	110	*
	1000°F	700	75	*	**226**	*	>600	*	127	*	>600	500	85	0.2
	1000°F	500	125	*	**119**	*	>600	425	91	0.3	>600	350	61	0.2

Table 4-4.3-2 Recommended Sample Tube Sizes for Pressures ≤ 400 psia (Cont'd)
(Used with permission — Sentry Equipment Co.)

Pressure, psia	Condition	Sample Flow, cc/min	½-in. O.D. × 0.83 in. Wall				⅝-in. O.D. × 0.083 in. Wall				¾-in. O.D. × 0.095 in. Wall			
			Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec	Max. L, ft	Cond. L, ft	Steam V_{max}, ft/sec	Cond. V_{min}, ft/sec
100	Saturated	900	N.R.	*	**241**	*	100	*	**180**	*	400	*	86	*
	Saturated	700	N.R.	*	**187**	*	200	*	**130**	*	>600	565	67	0.3
	Saturated	500	50	*	**172**	*	>600	490	71	0.3	>600	375	48	0.2
	1000°F	900	N.R.	*	**474**	*	125	*	**235**	*	350	*	165	*
	1000°F	700	N.R.	*	**366**	*	200	*	**174**	*	>600	*	128	*
	1000°F	500	N.R.	*	**259**	*	600	595	136	0.3	>600	440	91	0.2
87	Saturated	900	N.R.	*	**275**	*	75	*	**215**	*	250	*	**123**	*
	Saturated	700	N.R.	*	**214**	*	150	*	**178**	*	>600	*	77	*
	Saturated	500	50	*	**243**	*	450	*	81	*	>600	410	54	0.2
	1000°F	900	N.R.	*	**548**	*	75	*	**285**	*	225	*	190	*
	1000°F	700	N.R.	*	**422**	*	125	*	**177**	*	500	*	148	*
	1000°F	500	N.R.	*	**298**	*	275	*	157	*	>600	475	105	0.2

GENERAL NOTE:

Cond. L = length where all steam has been condensed. An asterisk (*) in this column indicates that the steam was not fully condensed in the maximum recommended length.

Cond. V_{min} = velocity of the condensate at a 500 ft (154 m) length. Since the density of water varies with temperature, any sampling tube shorter than 500 ft (154 m) would have terminal velocities slightly higher than this value; longer tubes would have slower velocities. As above, an (*) in this column indicates that the steam is not fully condensed in the recommended length or has not condensed within 500 ft (154 m).

Max. L = maximum recommended length of tube for that pressure and flow rate. An "N.R." in this column indicates that this size of sample tube is not recommended for any length since the compounded pressure drop is excessive.

Steam V_{max} = maximum velocity of the steam in the recommended length. A boldface value in this column indicates that the steam velocity is increasing due to expansion. Boldface values are taken at the maximum recommended length. The required initial steam velocity is shown for all values where the tube size is not recommended for any length.

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[3] Berry, W. E., and Diegle, R. B. "Survey of Corrosion, Generation, Transport, and Deposition in Light Water Reactors." EPRl NP-522, Final Report, March 1979.

[4] Coulter, Earl E. "Sampling Steam and Water in Thermal Power Plants." Presented at the Electric Utility Workshop at the University of Illinois, March 1988.

[5] Rommelfaenger, E. "Design Criteria for Steam Sample Lines." Presented at the EPRl Fourth International Conference on Cycle Chemistry in Fossil Plants, September 1994.

[6] Two Phase Flow Models for Sample Line Sizing, a computer program by Sentry Equipment Corp., Copyright 1995.

[7] Heitmann, H.-G. Glastech. Ber. 38(2): 41 (1965).

Section 5
Sample Conditioning

5-1 INTRODUCTION

The objective of water and steam sample conditioning is to modify and control sample temperature, pressure, and flow rate from the sample source to delivery for grab sampling or on-line analysis. This conditioning must be done safely and most importantly, achieved so as to ensure that the sample is truly representative of the system condition at the point(s) of sampling. Trace analysis (ppb-mg/L) requires special considerations to maximize the probability that measured results truly reflect the existing conditions in the system at the time of sampling.

Sections 3 and 4 discuss the proper methods for obtaining and transporting the sample. This Section discusses the requirements of various sample system components and their appropriate application and possible impact on sample quality. General reference is directed to ASTM standards providing additional information on this subject. [1–4]

5-2 DEFINITIONS

back pressure regulator: device designed to maintain a constant pressure upstream of itself (variable or fixed back pressure regulators are available) to maintain constant pressure to the analyzer flow control valves.

head cup: method used to achieve constant pressure (see back pressure regulator). Incorporates plumbing of the sample to a selected height above the analyzers to provide a constant inlet sample pressure. The sample flow is delivered to an elevated cup with an overflow to maintain constant head pressure to the analyzers as long as sample flow to the head cup is greater than the outlet flow to other analyzers and the grab sample.

NOTE: In recent years, highly sensitive back pressure regulators have become the standard method of sample pressure control. Sample pressure requirements and head height limitations also restrict application of the head-cup, pressure-control method, and therefore, it is not recommended.

pressure reducer: device designed to reduce pressure, and therefore control flow, of the cooled sample to a controllable pressure.

sample cooler: small heat exchanger (usually with a high pressure rating) used to cool sample streams.

variable rod-in-tube orifice: type of pressure reducer that uses a retractable, tapered rod inside a reamed tube to provide a variable orifice for pressure reduction parallel with sample flow while allowing retraction for cleaning of crud bursts.

5-3 MATERIALS

In high-purity sampling, the sampling lines and major sampling components within the sample conditioning system should be made of stainless steel when practical. Nonleaching plastics and glass components for measuring flow, holding resin, etc., can be used as required. Pressure and temperature ratings should be selected based on the specific service of the component.

NOTE: Some sample transport materials can be permeable to CO_2 and O_2. Care should be taken when selecting these materials.

5-4 VALVES AND FITTINGS

5-4.1 Isolation Valves

An isolation valve shall be located at the inlet to the sample conditioning system and/or at the sample cooler inlet. The valve rating shall be compatible with the pressure/temperature of the sample source. See Section 4 for information on root valves.

5-4.2 Pressure Reducers

Pressure reducers shall be located downstream of the primary sample cooler so that the liquid is sub-cooled before pressure reduction. For samples equal to or greater than 500 psig (3 447 kPa), the pressure reducer should be a rod-in-tube type orifice (variable or fixed) or a capillary tube. Variable rod-in-tube devices are recommended since they provide for varying the pressure drop and, therefore, the flow and are cleanable in-place. Also, this method of pressure reduction eliminates the possibility of sample bias due to the potential dissociation of water into hydrogen and oxygen that can occur across throttling valves when sampling at high pressures. [4]

Forepressure regulators are not recommended for large pressure reductions because of susceptibility to erosion, water dissociation, and wire drawing of the stem or seat. For samples less than 500 psig (3 447 kPa), the pressure reducer should be a needle valve or forepressure regulator. A needle valve is preferred since it will not oscillate with small pressure variations.

5-4.3 Pressure Regulators

Pressure and flow regulation for on-line analysis is essential for proper instrument performance and repeatability. This is achieved by establishing a constant pressure zone where the sample line feeds the analyzer branch lines. Because of the relationship of pressure and flow, this constant pressure zone ensures that each analyzer fed from this zone gets a constant flow rate independent of actions taken in the other branch lines, while maintaining constant flow in the main sample line. This is necessary for a representative sample (see Section 4). To achieve this constant pressure zone in conjunction with the upstream pressure reducer, a back pressure regulator (fixed or variable) is required. A head cup will provide the required constant pressure zone but is not recommended for sample pressure control upstream of the analyzers (see subsection 5-2).

NOTE: A forepressure regulator without a backpressure regulator or head cup is not recommended. A forepressure regulator alone cannot provide a constant sample line flow. Flow changes in the branch lines below the regulator result in the forepressure regulator closing or opening to maintain the analyzer inlet pressure thereby changing the main sample line flow. The sample ceases to be representative. Use of a backpressure regulator is the highly preferred method to achieve the constant pressure zone.

5-4.4 Blowdown Valves

Blowdown/flushing valves may be used to purge sample lines that are not in continuous service or where suspended-solids deposition affects the sample (see para. 5-10.2). The blowdown/flushing valve can be located prior to or after the sample cooler. If it is located after the sample cooler, it should be located downstream of the pressure reducer. The advantage of locating the blowdown/flushing valve after the sample cooler and pressure reducer is that this allows for full exercise of the pressure reducer and also flushes the sample cooler itself. This can be important in the analysis of trace metals. A regulating type valve rated for the sample source pressure and temperature should be selected for applications prior to the sample cooler. High-pressure service ball valves shall be used for blowdown/flushing after the sample cooler.

5-4.5 Other Valves

Other valves should be selected based on specific requirements and evaluated for their pressure/temperature service, e.g., analyzer flow metering, secondary isolation, grab sampling, sample sharing, etc.

5-4.5.1 Ball Valves. Ball valves are usually used for low-pressure blowdown, sample sharing, or other on/off applications where a diversion of sample flow is required. In some low-pressure sample applications, e.g., LP steam of a combined cycle plant, ball valves are sometimes used for isolation to reduce sample pressure drop when limited sample pressure is available.

NOTE: Selecting a ball valve for grab sample use without a flow metering valve in series with it can starve the constant-pressure zone created by the backpressure regulator and disrupt sample flow.

5-4.5.2 Sample Relief Valves. Each sample line should be provided with a method to protect components from overpressurization. Acceptable methods include suitable backpressure regulator with built-in relieving capacity, head cup or suitable relief valve located downstream of the pressure reducer, and primary sample cooler.

NOTE: If a relief valve is used, it shall be positioned so that no dead leg is present, thereby avoiding contamination of the flowing sample.

5-4.5.3 Cooling Water Valves On Sample Coolers. Each sample cooler should have an inlet (isolation) and outlet (throttling and isolation) valve. All cooling-water flow adjustments should be made with the outlet valve so that the maximum available cooling water pressure is available to the sample cooler.

CAUTION:
(1) **The sample cooler shell needs to be protected from overpressurization if it is inadvertently isolated when sample flow is present or the sample tube ruptures. The design of the piping shall provide a means of drainage or expansion of the cooling water should these conditions occur. Recommended methods include a three-way diverting ball valve installed such that the flow to the shell cannot be isolated (cooling water or relief/vent) or a relief valve installed between the cooler shell and the isolation valve.**
(2) **Loss of cooling water flow can cause serious damage and corrosion and become a safety hazard.**

5-4.6 Fittings

It is always preferable to use bends rather than fittings to change direction of sample tubing. Compression or socket weld fittings for sample lines should be selected based on application and servicing needs. Because improperly welded joints are susceptible to plugging by suspended solids, compression fittings are preferred.

5-4.7 Thermal Protection Devices

To ensure operator safety and prevent analyzer failure due to overheating, the addition of a thermal protection device to interrupt sample flow if an overtemperature condition occurs is highly recommended. Self-contained temperature control valves with a manual reset feature, or temperature controllers with an appropriately rated automatic shutoff valve, are the preferred methods of providing this protection. Some remote indication of this event (contact closure to an alarm and/or computer system) is also recommended.

5-5 SAMPLE COOLERS

High-efficiency sample coolers used for primary temperature reduction/condensation shall be designed for

the pressure/temperature of the sample source. They should be capable of reducing the incoming sample temperature to within 5°F (2.8°C) of the cooling water inlet temperature for water samples and 10°F (5.6°C) of the cooling water inlet temperature for steam samples at representative sample flows. Cooling water requirements should be as low as possible to conserve water resources and cost. Sample coolers used for secondary cooling shall be capable of a 1°F (0.5°C) approach to the chilled water temperature. The tube through which the sample will flow shall be continuous.

The cooler tube shall be made of stainless steel, preferably AISI 316. Specific water chemistry could dictate different materials for improved corrosion resistance, e.g., Alloy 600 series for high chlorides in the cooling water. The sample-cooler shell containing the cooling water should be designed to provide adequate cooling water velocity to achieve required sample-cooler efficiency as noted above and be made of material that is corrosion resistant to the cooling water in use. Materials that have corrosion resistance to the ambient atmosphere around the sample cooler should also be considered to avoid exterior corrosion.

5-6 FLOW METERS

A visual means of reading and setting total and analyzer branch sample flow(s) is essential. Rotameters or other mechanical or electronic flow-measuring devices are suitable. The rotameter shall be made of materials that are corrosion resistant and not reactive with the sample. For total sample flow, this is the only way to ensure that the sample is flowing at a velocity that ensures a representative sample. Glass-tubed rotameters are preferred by most users over plastic because they require less frequent cleaning and can be replaced/upgraded by only replacing the glass tube.

NOTE: Care should be taken during installation and maintenance to ensure that there is no air in-leakage from the flow-measuring device.

5-7 SAMPLE FILTERS

Sample filters can trap particles and may reduce plugging but also affect sample analytical results and are not recommended. Proper sample-system design and representative flow should avoid plugging problems. Use of sample filters should, therefore, be closely evaluated and, if found necessary, only be installed in the specific analyzer branch line needing filtration.

5-8 PRESSURE AND TEMPERATURE GAGES

Gages of the appropriate material and service ratings should be strategically used to verify sample temperature and pressure in the sample system. Ranges should

be selected so that normal readings are between 30% and 70% of full scale.

5-9 PUMPS

Samples of hotwell condensate and other low-pressure water and/or steam (after condensing) samples may likely require the use of a pump to provide adequate sample pressure. Small centrifugal pumps (sealless or canned), magnetically coupled gear pumps, or diaphragm pumps using stainless steel construction are acceptable. Capability to handle low Net Positive Suction Head (absolute) [NPSH(A)] is required.

5-10 SAMPLE CONDITIONING METHODOLOGY

5-10.1 Typical Sample Line

Figure 5-10.1 shows a typical sample line for high-pressure service. A low-pressure line [below 500 psig (3.45 MPa)] would be similar, except a needle or metering type valve would be substituted for the pressure reducer.

This typical component lineup provides for complete sample conditioning for pressure, temperature, and flow, ensuring a highly representative sample. See notes to Fig. 5-10.1 for additional information.

5-10.2 Sample Line Flushing

The sample system requires high-velocity flushing during system startups to remove the potentially large amounts of suspended material that often enter the sample system during this operational phase. The sample system should be designed to minimize this flushing process in both base load and cycling modes. Proper sample line size, short sample lines, and the capability for the high-velocity flushing noted above are essential. If a sample system design cannot provide the sample flow velocity that maintains a clean and stable system in normal operation, then provision shall be made for periodic high-velocity flush to minimize deposition of suspended solids.

If sample flow velocity is low, as a result of a throttled valve or other restriction, concentrated slugs of suspended particulate can form a plug at these locations and cause total sample flow stoppage. This is a common problem during process system startup. Nearly all sample system pluggage can be prevented by a sample system design that provides the means for a short and unrestricted sample-flush flow path from root valves to the grab sample sink (blowdown valve after sample cooler), bypassing on-line analyzers and secondary sample coolers.

NOTE: On-line analyzers should be isolated to prevent particulate fouling during system startup.

5-10.2.1 Suggested Startup Procedure for Sampling System.   The simple but useful procedure of beginning

Fig. 5-10.1   Typical Sample Line for High-Pressure Service

AE-1 = analytical element with effluent to waste
AE-2 = analytical element with effluent to recovery
BPR/RV = back pressure regulator / relief valve
F.I. = total flow indicator
FICV = valved flow indicator(s) / controller(s)
P.I. = pressure indicator
RV-1 = cooling water header relief valve
SC-1 = primary sample cooler
SC-2 = secondary sample cooler
T.I. = temperature indicator
TSV = thermal shutoff valve
TW = thermowell
V-1 = sample isolation valve
V-2 = cooling water throtting / isolation valve
V-3 = cooling water diverting / isolation valve
V-4 = high-pressure pressure reducer
V-5 = low-pressure pressure reducer
V-6 = three-way sample blowdown valve
V-7 = pressure gage isolation valve

GENERAL NOTES:
(a) If the combination BPR / RV is not used,
    a sample relief valve upstream of the
    last valve that can be isolated must be
    included.

(b) Cooling water isolation for primary sample
    cooler can be accomplished as shown or in
    other ways. Isolation method must allow for
    shell side relief of the sample cooler.

(c) High-pressure blowdown at the sample
    panel inlet is also acceptable but does not
    allow blowdown of the primary sample
    cooler and pressure reducer.

(d) Secondary sample cooler does not normally
    require chilled water isolation valves.
    Isolation valves can be added if required.

21

each startup by flushing each sample line to the sample sink provides an awareness of materials being carried from the sample system during startup.

CAUTION: When performing a high-velocity flush of high-pressure samples, primary sample cooling capacity may be temporarily exceeded. It is necessary to monitor the sample outlet temperature from the primary sample cooler and reduce flushing flow before outlet temperatures become excessive. While no generally agreed flush rate is available, flushing at a rate of approximately 125% of normal flow is usually adequate to flush sample lines of old sample after intermittent shutdown. Since steady-state erosion/deposition might not be reached for some time period after flushing, short sample lines are most critical in cycling operations to improve sample accuracy.

(a) Temporarily isolate sample flow to on-line analyzers to protect them against particulate fouling.

(b) Position the three-way sample ball valve to route sample flush to the sink.

(c) The sink area receiving the sample should be clean and polished free of stains to aid detection and visual evaluation of small amounts of entrained solids.

(d) Open the pressure reducer at the outlet of the primary sample cooler. Monitor sample line temperature.

(e) Expect to see a darkening of the sample discharge to the sink as particulate is released in the sample line. Observing the sample-line flush to the sample sink is useful in evaluating flushing characteristics of the sample line.

(f) When the sample clears, continue the flush for several volume changes or as the primary sample cooler outlet temperature permits. Reduce the bulk sample flow to normal, close the flow-adjusting valve, reposition the three-way ball valve to route normal sample flow to on-line analyzers, and commence normal sample system operation.

(g) Verify that the sum of sample flows to analyzers and bypass to recovery or waste is sufficient to achieve the desired 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s) velocity in the sample line or, if this is not achievable, the maximum sustainable sample flow rate the system will deliver (see Fig. 5-10.1).

As noted earlier, a sample line designed for sample velocity in the range of 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s) is in a constant state of flush during normal operation and contributes to minimal sample bias. The possibility of sample-line plugging during startup conditions is minimized by proper valve alignment to avoid flow restrictions during sample-line startup and flush.

Sample drains shall be sized to accommodate the total amount of wastewater exiting the panel during sample flush operations to ensure on-line monitors are unaffected.

5-10.3 Establishing and Verifying Sample-Line Flow and Conditioning

To determine proper sample-line flow based on line size and recommended sample velocity, see Section 4.

Once the proper main-line sample flow is known, the flow is achieved by adjusting the pressure reducer until the flowmeter reads the required flow. Verify that the backpressure regulator is operating properly by adjusting downstream flow in one of the branch analyzer feed lines. As this flow is adjusted, the main line sample flow should not vary (see para. 5-4.3.) Check that the primary cooler is adequately reducing the sample temperature at the established flow rate. Cooling water temperature and flow to the cooler should be checked if the sample outlet temperature is too high. Ensure that the secondary cooling system is receiving an adequate flow of chilled water.

5-10.4 Importance of Secondary Cooling

Secondary sample coolers provide trim cooling of samples to the standard temperature of 77°F (25°C) prior to on-line analysis and grab sample collection. This is the only way to ensure repeatable and accurate results, especially for pH and conductivity at low levels of analytical sensitivity. On-line analyzers typically include temperature compensation to correct for sample temperature variations and algorithms to estimate corrections for high purity water chemistry.

However, this compensation may not provide proper correction for varied water chemistries and is highly dependent on the accuracy of the temperature measurement itself. [5] For these reasons and greatest accuracy, trim cooling should be accomplished to within ±1°F of standard temperature. This, when coupled with automatic temperature compensation in the analytical instrument, will minimize temperature-induced bias in the measurements.

NOTE: Laboratory instruments usually require manual correction for water chemistries even when equipped with automatic temperature compensation.

Secondary or trim sample coolers should be individual coolers as detailed in subsection 5-5. Chilled cooling water shall be treated with demineralized water supplied from a precision temperature-controlled chilled water system. Although secondary cooling coils can be immersed in a water bath with high-volume chilled water flow, accurate temperature control is not easily achieved unless all incoming samples are near the same temperature.

5-10.5 Grab Sampling

The grab sample should be taken from the same continuous flowing stream that feeds the on-line analyzers, i.e., the constant-pressure zone detailed in para. 5-4.3. A separate branch line with a metering valve and on/off ball valve may be used to take the grab sample. Another method, which ensures a continuously flowing sample with no dead legs, is to use the discharge of the backpressure regulator. In addition to providing a grab

sample in a state of continuous rinse, this method reduces components and system cost.

5-10.6 Analyzer Verification (Patch Panel)

Quick connects provide the capability of switching samples from one on-line analyzer to another. Quick connects allow the operator to

(a) Verify analyzer performance by switching two different samples to their opposing analyzers (e.g., verify hotwell and economizer pH monitors by switching hotwell and economizer samples).

(b) Perform simultaneous routing of a high-purity sample to two similar analyzers to set relative zero settings during calibration (e.g., split a condensed saturated steam sample to two sodium analyzers to establish low-end calibration in the 1.0 ppb range).

(c) Reroute sample to an alternate analyzer in the event of instrument failure.

The use of a quick-connect patch panel for instrument verification and extended monitoring provides simple but highly effective trouble shooting and quality assurance evaluation of on-line instrumentation. Cross-connecting to an alternate analyzer for signal verification requires spare, extended length connecting tubes for these special occasions.

NOTE: Flexible tubing can affect sample (see subsection 5-3).

CAUTION: When quick connects are used to interchange water samples to on-line analyzers, this information must be duly noted on data loggers and continuous recorders.

5-11 BIBLIOGRAPHY

The following sources were cited using numbered references throughout this Section:

[1] Practice for Sampling Steam, ASTM D 1066.

[2] Practice for Sampling Water in Closed Conduits, ASTM D 3370.

[3] Practice for Flow Control and Temperature Control for On-line Water Sampling and Analysis, ASTM D 5540.

[4] Dickinson, N. L., Keilbaugh, W.A., and Pocock, F.J. "Some Physio-Chemical Phenomena in Super-Critical Water." ASME Paper No. 58-A-267.

[5] Morash, K. R., Thornton, R. D., Saunders, C. H., Bevilacqua, A. C., and Light, T. S. "Measurement of the Resistivity of High-Purity Water at Elevated Temperatures." Ultrapure Water (December 1994) 18-22.

Section 6
Sample Analysis and Instrumentation

6-1 INTRODUCTION

The purpose of this Section is to provide general definitions, applicability, and analytical methods for the sampling criteria detailed in Section 2, as well as other analytical techniques and methods that may be used on a case-by-case basis. Analyses reviewed and suggested in this Section should not be construed to be the only methodology available to achieve the results or determine system performance. Information on analytical methods is found in each definition. Other methods might be available, and local analytical chemistry specialists can and should be consulted to determine specific requirements.

6-2 DEFINITIONS

In this Section, various terms relating to water analysis will be used that may not be familiar to the reader; therefore, definitions of these terms are being provided in the following paragraphs:

AVT: all volatile treatment, usually meaning treatment composed of ammonia, morpholine or other neutralizing amines, and hydrazine or other volatile oxygen scavengers, which leave no solids on evaporation. See subsection 2-3 for further discussion of AVT variations.

chemical absorption spectrophotometry: quantitative procedures devised to relate light absorption at a selected wavelength to the concentration of the species of interest in the optical path.

electrical conductivity: the reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature.

flame emission spectroscopy: a flame photometric technique in which a solution containing the sample to be analyzed is optically excited in an oxyhydrogen or oxyacetylene flame. Relaxation of the atomized particles to their ground states produces emission spectra that serve as the basis for qualitative and quantitative analysis. Emission spectra can arise from several types of particles, including atoms, ions, small molecules, and radicals.

furnace atomic absorption spectroscopy: an analytical technique based on the absorption of electromagnetic radiation by atomic particles. This technique, along with other spectral methods, requires that the sample be atomized, a process in which the sample constituents are decomposed and converted to gaseous elementary particles (atoms or ions). The absorption spectrum of the resulting atoms or ions then serves as the basis for qualitative and quantitative analysis for the elements contained within the sample. Furnace AA spectroscopy uses an electrothermal method of sample atomization. This type of atomization provides enhanced sensitivity compared with flame methods of atomization.

integrated sampling: the practice of passing a water sample through a filter and/or ion exchange membrane to retain and concentrate particulate and/or ionic materials (primarily corrosion products) from the sample for subsequent analysis. Both the flow rate and duration of sampling period are recorded to allow calculation of concentrations.

ion exchange: a reversible process by which ions are interchanged between an insoluble material and a liquid. Ion-exchange material has the ability to exchange reversibly certain ions in its structure or attached to its surface as functional groups, with ions in surrounding medium. These ion-exchange materials may be cationic or anionic and are capable of reversible exchange of positively or negatively charged ions, respectively.

ion exchange membrane: a membrane made from an ion-exchanging polymer for the purpose of removing ion constituents from aqueous solutions. The use of ion exchange membrane requires the transfer of ions to the membrane polymer, which returns an equivalent number of ionic species stored on the membrane.

ion selective electrode: an analytical technique for measuring ionic constituents primarily in aqueous solutions. This technique is based on the measurement, using a specific ion meter, of an ion exchange potential that is developed at the active surface of the electrode. The potential varies with the logarithm of the concentration of ions in the sample. Common examples are pH, sodium, and chloride electrodes.

membrane filter: a membrane used in a separation process for water purification or as an analytical device for the detection of suspended solids or dissolved ionic constituents.

oxygenated treatment: a water treatment technique used primarily for supercritical and subcritical once-through, fossil-fired boilers. This treatment involves the use of

24

oxygen at near neutral or slightly alkaline pH in high-purity condensate/feedwater (<0.15 μS/cm cation conductivity). The principal advantage of the treatment is the reduction of preboiler corrosion and a subsequent reduction in transport of corrosion products to the boiler.

timesharing: a single analyzer receiving two or more separate sample streams on a time-share basis.

TOC: Total Organic Carbon (see para. 6-2.22).

6-2.1 Test Method Details

Test methods listed do not include descriptive information regarding common laboratory equipment, such as beakers, graduated cylinders, volumetric flasks, crucibles, casseroles, Erlenmeyer flasks, etc., as it is assumed that the laboratories using this text will be well supplied with such equipment.

NOTE: Listed ASTM standards [1] include precision and bias statements in each method. For other methods, ASME cannot comment on the precision and bias of the listed equipment. ASTM standards identified by an asterisk have been withdrawn for various reasons; however, copies are still available from ASTM, and they may provide valuable background information for establishing an appropriate test method.

6-2.2 Purity of Water and Reagents

purity of reagents: ACS reagent grade chemicals shall be used in all tests, where such specifications are available. Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. See ASTM Standard Practice E 200 for further details and preparation, standardization, and storage of standard solutions.

purity of water: unless otherwise indicated, references to water shall be understood to mean Type II reagent water conforming to ASTM Specification D 1193. Essentially, Type II is described as having maximum electrical conductivity of 1.0 μS/cm at 25°C, although other qualities, such as TOC, sodium, chlorides, and total silica, may also be specified. Type II rather than Type Ill has been specified mainly to qualify as reagent water to be used in determining low levels of silica (10 mg/L). The user should consult the analytical method for the proper reagent water quality required.

6-2.3 Sample Guidelines

Reference Sections 3, 4, and 5 regarding appropriate sample conditioning and transport procedures to ensure representative sample quality.

6-2.3.1 Grab Sample Analysis. Grab samples should be taken from continuously flowing streams and not from any dead leg in the sample conditioning system. Prior to grab sample analysis for metals, blowdown of the sample line in accordance with the procedures detailed in Section 5 should be conducted.

While a grab sample represents the conditions existing only at the point and time of sampling, it shall be the goal of the sampler to collect a sample that is representative of the main body of the water sampled. The necessary details to extract this representative sample are described in Section 2. It should be recognized that there are a number of critical factors necessary to achieve a representative sample, namely point of sampling, time of sampling, equipment used in extracting the sample, proper sample line design (see Section 4), and sample conditioning (see Section 5).

6-2.3.2 On-Line Sample Analysis. On-line chemical analysis requires proper sample conditioning, particularly constant flow, to ensure the repeatability and accuracy of the analysis. Constant sample temperature also improves all on-line analysis.

On-line sample analysis (continuous and/or integrated methods of sampling) has the advantage of showing continuous analytical results to reveal normal operating trends and rate/range of upset or abnormal conditions.

On-line analyzers should be checked for accuracy on a regular basis and be calibrated in accordance with manufacturer recommendations. Manufacturers of on-line analyzers will generally specify a flow rate range and maximum pressure for proper equipment operation. Ensure that these requirements, in addition to constant flow and regulated temperature of the sample, are met. Applicable practices for sampling include ASTM D 1066, D 3370, D 5540, and D 4453.

6-2.3.3 Time Sharing of Instruments. Time sharing is the use of a single analyzer receiving two or more separate sample streams on a time share basis. Some benefits include the following:

(a) Time sharing of samples reduces the number of analyzers required to monitor a system, eliminates possible error between analyzers, and provides a comparison of relative values between two or more streams. For example, a single sodium analyzer, alternating between condensate polisher inlet and outlet, can resolve the onset of exhaustion with fractional ppb precision. This is not possible with two independently calibrated analyzers.

(b) Colorimetric analyzers are subject to upscale "zero" drift, generally caused by colorimeter cell fouling. Time sharing boiler water samples with steam and/or feedwater samples allows assessment of instrument performance by visual inspection. This will identify relative zero and expose zero shift when both values migrate upscale by equivalent amounts. Relative zero can be reestablished without removing the analyzer from service.

For this example, a silica analyzer monitors boiler water, while an adjacent hydrazine analyzer monitors feedwater. Automatic switching of samples on a timed

cycle allows boiler water silica to be rinsed down with feedwater to relative zero while the hydrazine analyzer rinses down with boiler water to a relative zero hydrazine value.

(c) Some examples of samples that benefit from time sharing the same analyzer are as follows.

(1) sodium

(a) condensate pump discharge vs. condensate polisher outlet

(b) condensate polisher outlet vs. saturated steam

(c) demineralizer water makeup vs. saturated steam

(2) silica

(a) boiler drum water vs. feedwater

(b) demineralizer mixed bed effluent vs. strong base anion effluent

(3) hydrazine and silica

(a) feedwater and boiler water alternately cycle to hydrazine and silica analyzers

The following are time shared in order to achieve the precision between samples necessary to detect differences that would otherwise be masked by the normal range of variation of independent analyzers:

(a) dissolved oxygen

(1) low-pressure heater drains vs. condensate pump discharge

(2) deaerator inlet vs. deaerator outlet

6-2.3.4 Data Collection. Results from both grab sample and on-line analysis at time of sampling should be collected and logged to provide for trending and comparison. The quality of samples can change dramatically during system startup, and therefore, an ongoing logging of information is critical to observe these trends. See Section 7 for specific details on appropriate data collection.

6-3 ANALYSIS, DEFINITIONS, AND APPLICATIONS

The purpose of this subsection is to provide generic definitions, typical applicability, and methods for various types of analysis.

6-3.1 Alkalinity (Hydrated)

The quantitative capacity of aqueous media to react with hydrogen ions. Routine testing of boiler water alkalinity is used to help set levels of chemical treatment to control scale, corrosion, and other adverse chemical conditions. The combination of alkalinity and pH indicates the buffering capacity of the sample (see Table 6-3.1).

6-3.2 Amines (Neutralizing)

Organic compounds of varying molecular weight that contain an amine (–NH or –NH$_2$) group. Organic amines

are most commonly used in nuclear, industrial, and low-pressure fossil cycles. Various amines have differing vapor/liquid distribution ratios and base strengths.

The distribution ratios and base strengths vary with temperature. [2, 3] Two or more amines, because of their differing vapor-to-liquid ratios, may be used in industrial systems to neutralize carbonic acid and maintain proper pH throughout the process. Since the distribution ratio, pH, and decomposition rate vary with temperature, the user must consider these parameters for the proper application of neutralizing amines. Neutralizing amines may not be permitted to treat water in industrial processes involving food, beverages, pharmaceuticals, and hospitals. They are often not measured directly, but rather, the dosage is adjusted to maintain proper pH. Ion and gas chromatography may be used for direct measurement (see Table 6-3.2).

NOTE: Decomposition products for all amines have not been identified. Ammonia has been the only acceptable pH additive for high-pressure fossil once-through systems.

6-3.3 Ammonia

Highly soluble alkaline compound of nitrogen and hydrogen. Typically present as the ammonium ion. Ammonium hydroxide is used in power plant cycles for pH control. Regulating the amount of ammonia necessary to stay within the prescribed limits is especially important in units with mixed metallurgy. Ammonia is normally injected into the cycle at the condensate pump discharge and monitored at the economizer inlet using either pH or conductivity as the major control mechanism. Concurrent with the feed of ammonia, hydrazine is often fed to the cycle to control dissolved oxygen.

Breakdown products resulting from thermal decomposition of hydrazine are nitrogen and ammonia. Most of the ammonia vaporizes in the boiler water and carries over with the steam. On occasion, ammonia levels in the condensate can reach unacceptably high levels and (especially in the presence of dissolved oxygen) become extremely corrosive to the copper and copper-alloy equipment in steam condensing and preboiler systems (see Table 6-3.3).

6-3.4 Carbon Dioxide

Compound CO_2, which makes up about 0.03% by volume of the atmosphere. It readily dissolves to form carbonic acid and related bicarbonate species in water. Pure water in equilibrium with air has a pH of about 5.6 and a conductivity of about 1 μS/cm. CO_2 can deplete polisher resin and be corrosive, especially in wet stages of turbine and steam piping (see Table 6-3.4).

Carbon dioxide may be detected by measuring the difference between cation and degassed cation conductivity values (see para. 6-3.6).

26

Table 6-3.1   Alkalinity

Method	Usage: On-Line	Usage: Grab	Comments
Electrometric titration (ASTM D 1067 A hydroxide ion in water)	. . .	X	. . .

Table 6-3.2   Amines (Neutralizing)

Method	Usage: On-Line	Usage: Grab	Comments
Vendor-specific instruments	X	X	. . .
Ion chromatography, (ASTM D 1942) [Note (1)]	X	X	. . .
Gas chromatography, (ASTM D 4983) [Note (1)]	X	X	. . .

NOTE:
(1) Withdrawn method but still available (see para. 6-3.11).

Table 6-3.3   Ammonia

Method	Usage: On-Line	Usage: Grab	Comments
Direct nesslerization (ASTM D 1426 A)	. . .	X	Recommended technique, especially for grab samples
Ion selective electrode (ASTM D 1426 B)	X	X	. . .
Ion chromatography, (ASTM D 6919)	. . .	X	. . .
Vendor-specific instruments	X	. . .	. . .

NOTE:
(1) Withdrawn method but still available (see Subsection 6-1.2).

Table 6-3.4   Carbon Dioxide

Method	Usage: On-Line	Usage: Grab	Comments
Titrimetric and gas-sensing electrode (ASTM D 513)	. . .	X	. . .
Conductivity (ASTM D 4519)	X	. . .	. . .
Ion chromatography	X	X	. . .
Vendor-specific instruments	. . .	. . .	Some TOC instruments are capable of CO_2 measurement

6-3.5 Chloride

Anion of the halogen family (Cl^-). Chloride is one of the most aggressive anions in causing corrosion. Chloride intrusions commonly result from condenser leaks and sometimes condensate polishing or makeup demineralizers. The resultant ingress of chloride can participate in pitting and stress corrosion cracking of major steam cycle components. Ultimately, it can reach the turbine as a result of mechanical or vaporous carryover, with potential damage to blade materials. While cation conductivity can sometimes indicate the presence of chloride, this measurement usually includes larger effects from other less aggressive species, such as carbon dioxide, unless degassed cation conductivity is used (see Table 6-3.5).

6-3.6 Conductivity

6-3.6.1 Conductivity, Specific. A measurement of all ionic species that contribute to the electric conductivity of a solution. In essence, conductivity is a broad measurement of total ionic impurities. Normally reported as micro-siemens per centimeter, it is electrically noted as the reciprocal of the resistance in ohms measured between opposite faces of a cubic centimeter of an aqueous solution referenced to 25°C.

Most modern analyzers attempt to temperature-compensate; however, accurate temperature compensation of high-purity conductivity measurement must account for the dramatic change in ionization of water with temperature. On samples with ammonia, morpholine, etc.,

Table 6-3.5   Chloride

Method	Usage: On-Line	Usage: Grab	Comments
Ion selective electrode	X	...	Lowers sample pH and temperature to achieve $\mu g/L$ (ppb) sensitivity
Ion selective electrode (ASTM D 512 C)	...	X	mg/L (ppm) concentrations only
Ion chromatography (ASTM D 5542)	...	X	...
Ion chromatography (ASTM D 5996)	X	...	...

Table 6-3.6.1   Specific Conductivity

Method	Usage: On-Line	Usage: Grab	Comments
Electrical probe (ASTM D 1125)	...	X	...
Electrical probe (ASTM D 5391)	X	...	Recommended

present, and for cation conductivity samples (para. 6-2.6.2), specialized compensation algorithms must include their unique effects on the ionization of water. [4, 5]. For best results, sample temperature should be controlled to 77°F (25°C) (see para. 5-10.4).

Electrical conductivity methods are widely used for monitoring makeup water, feedwater, and condenser leakage. Advantages are the comparatively little maintenance required for the sensors (cells), low cost, and high reliability.

Specific conductivity, in responding to all ions present, tends to follow the concentration of pH-adjusting reagent(s) (usually ammonia), since that is the dominant material present in samples under normal operation (see Table 6-3.6.1).

6-3.6.2 Conductivity, Cation (Acid Conductivity, Hydrogen Cation-Exchanged Conductivity, or Conductivity After Strong Acid-Cation Exchange). Similar to specific conductivity, cation conductivity is a measurement of anionic contamination rather than total ionic species. This is the case since the sample is passed through a strong acid cation exchange resin before conductivity measurement, where ammonia, amines, and other cationic contaminants are removed. This greatly sharpens sensitivity to contamination by removing the masking effect of ammonia and amines and simultaneously converting salts to the corresponding mineral acids, which are considerably more conductive than the salts, thus further increasing sensitivity.

Cation conductivity is particularly useful for detecting the leakage of cooling water into condensate. Most dissolved salts found in natural waters, plus dissolved acidic gases (e.g., CO_2) will contribute to acid conductivity. However, nonionized or weakly ionized substances (e.g., SiO_2) will not be detected by this method. Hydroxide ions are not measured by this method (see Table 6-3.6.2).

6-3.6.3 Conductivity, Degassed Cation. This technique uses strong acid cation exchange and degasification, which provides the means to determine conductivity due to anionic impurities without the influence of carbon dioxide. The sample is passed first through a column of cation resin in the hydrogen form, then through a degassifier, such as an electric reboiler, with final measurement of the electrical conductivity of the total anions free of interference due to amines and carbon dioxide. Consistent reboiler degassing, especially at low conductivity levels, depends on stable sample flow rate, close temperature control, consistent steam venting, etc. [6] (see Table 6-3.6.3).

Most large turbine condensers receive, in addition to exhaust steam, the makeup water, drips, drains, and vent discharges from other components in the steam plant. Impaired purity of one or more of these flow streams may increase the conductivity of the condensate. In the absence of other information, the interpretation could well be leakage of cooling water. Persistence of high conductivity after such flow streams are isolated from the condenser is more certain evidence of in-leakage. Simultaneous measurements of the sodium, specific conductivity, cation conductivity, cation conductivity after CO_2 removal, hardness, and pH of both condensate and throttle steam may help distinguish sources of contamination.

6-3.7 Copper

Trace transition metal primarily present as soluble oxide. Copper alloys are frequently used for heat transfer components. Dissolved copper, usually as an oxide, is present as a corrosion product that can form deposits on heat transfer surfaces and turbines with attendant loss of efficiency. pH, ammonia, and dissolved oxygen are controlled to minimize corrosion of copper alloys. Monitoring copper levels provides feedback on the success of this control (see Table 6-3.7).

Table 6-3.6.2   Cation Conductivity

Method	Usage: On-Line	Usage: Grab	Comments
Electrical probe (ASTM D 6504 and D 5391)	X	...	...

Table 6-3.6.3   Degassed Cation Conductivity

Method	Usage: On-Line	Usage: Grab	Comments
Degasification and electrical probe (ASTM D 4519)	X	...	...

Table 6-3.7   Copper

Method	Usage: On-Line	Usage: Grab	Comments
Neocuproine colorimetric	...	X	...
Atomic absorption, direct (ASTM D 1688 A)	...	X	Over 50 μg/L
Atomic absorption, chelation-extraction (ASTM D 1688 B)	...	X	Over 50 μg/L
Atomic absorption, graphite furnace (ASTM D 1688 C)	...	X	Recommended 5–100 μg/L

Table 6-3.8   Dissolved Oxygen

Method	Usage: On-Line	Usage: Grab	Comments
Electrochemical (ASTM D 5462)	X	...	...
Color comparator using glass ampoules (ASTM D 5543)	...	X	...

NOTE: See para. 6-4.1 for information on integrated sampling techniques for copper.

6-3.8 Dissolved Oxygen

Oxygen gas dissolved/entrained in aqueous media. At high temperatures, especially with elevated conductivity, oxygen reacts readily with most metals. This corrosive attack not only weakens system components but also forms sludge, which can deposit on heat transfer surfaces and turbine blades. Control of dissolved oxygen is extremely important in any boiler cycle.

While most applications reduce dissolved oxygen concentration as low as possible, oxygenated treatment water chemistry maintains levels of 50 μg/L to 150 μg/L (ppb) to maintain ferrous metal passivation (see Table 6-3.8).

6-3.9 Hydrazine

Chemically known as N_2H_4, hydrazine is a powerful reducing agent used in boiler feedwater treatment as an oxygen scavenger and metal passivator. It is normally introduced into the cycle at the condensate pump discharge to provide a residual greater than or equal to three times the dissolved oxygen concentration. Hydrazine reacts with dissolved oxygen to form water and nitrogen.

WARNING: **Hydrazine vapors are a suspected carcinogen, and a threshold limit has been set by OSHA.**

In addition to reacting with dissolved oxygen to form water and nitrogen, hydrazine may also thermally decompose to form ammonia and nitrogen. Ammonia increases the pH and under certain conditions is corrosive to copper alloy components in the system. Therefore, the concentration of hydrazine must be maintained at a level that will scavenge the dissolved oxygen yet not increase ammonia levels so as to exceed guidelines for this parameter.

Hydrazine concentrations in the cycle water are measured at the deaerator inlet with a desired concentration of at least 20 ppb. Sometimes trace quantities are detected in the boiler water, depending upon cycle temperatures. Hydrazine is sometimes injected into the low-pressure turbine at the crossover pipe between the intermediate and low-pressure sections. Iron and copper concentrations may be reduced in samples from units that have injected hydrazine in this manner (see Table 6-3.9).

Table 6-3.9 Hydrazine

Method	Usage: On-Line	Usage: Grab	Comments
Colorimetric (ASTM D 1385)	...	X	May be used for online measurements
Ion selective electrode	X	...	...

Table 6-3.10 Hydrogen

Method	Usage: On-Line	Usage: Grab	Comments
Thermal conductivity	X	...	...
Fuel cell	X	...	...
Polarographic	X	...	...

6-3.10 Hydrogen

Increases in the hydrogen content of the steam or water may indicate accelerated corrosion of a component. On-line monitoring of hydrogen has been used to investigate corrosion of carbon-steel support plates in nuclear recirculating steam generators, a variety of corrosion mechanisms in fossil-fired boilers, dissolved hydrogen concentrations in PWR reactor coolant, and heavy water-moderated reactors. On-line instruments based on the principles of thermal conductivity, fuel cells, and polarography have been used, along with gas chromatographic analysis of grab samples. [7–11]

Extreme care should be taken in the interpretation of the data since hydrogen can be produced from sources other than corrosion, e.g., decomposition of hydrazine, morpholine, and organic chemicals; permeation through tube walls from external sources; and dissociation from throttling high-pressure steam (see Table 6-3.10).

6-3.11 Ion Chromatography

A form of high-pressure liquid chromatography (HPLC) in which ionic constituents are separated by ion exchange. Ion chromatography is commonly used for the determination of anions and cations but can also be used for organic acids. There are basically two types of ion chromatography (IC): suppressed IC and nonsuppressed IC.

Suppressed IC can be accomplished using either chemical or electrolytic suppression technology. In a chemical suppression example determining anions, a measured volume of sample is injected into a stream of flowing eluent, which usually consists of a carbonate/bicarbonate mixture or an electrolytically generated hydroxide solution. The eluent carries the sample through a column packed with anion exchange resin. The anions in the sample are separated in the column and elute at different times. As the anions subsequently move through the suppressor device (usually cation exchange resin), their counter ions (such as sodium) are removed and replaced with more conductive hydrogen ions, allowing for very sensitive detection of trace anions. In addition, the eluent cations are removed, which suppresses the background conductivity, further enhancing the signal-to-noise ratio. Anions measured at trace (μ/L) levels include fluoride, acetate, formate, chloride, nitrate, phosphate, and sulfate in high-purity water. A variation of chemical suppression is electrolytic suppression in which the conversion of eluent and analyte are done using an electrolytically regenerated suppression device that can simplify operation.

Nonsuppressed IC, also called electronically suppressed IC (not to be confused with electrolytic suppression above), is the method of simply shifting the base line of the chromatograph to subtract the background conductivity of the eluent. Electronic suppression typically produces negative peaks, and the polarity of the signal is often reversed so that the peaks are shown as positive (see Table 6-3.11).

6-3.12 Iron

Transition metal. Ferrous form (Fe^{2+}) can exist in oxygen-free water. Ferric form (Fe^{3+}) is readily formed under oxidizing conditions.

Steel can be used in boiler-cycle components only because it forms a thin film of magnetite (Fe_3O_4), ferric oxide hydrate ($FeOOH$), or hematite (Fe_2O_3), which protects against further corrosion. However, the solubility of these oxides is dependent on temperature and pH. Iron oxides are probably the most prevalent corrosion products and tend to form sludge and deposits that greatly reduce efficiency (see Table 6-3.12).

NOTE: See para. 6-4.1 for information on integrated sampling techniques for iron.

6-3.13 Morpholine

See amines.

Table 6-3.11   Ion Chromatography

Method	Usage: On-Line	Usage: Grab	Comments
Chemically suppressed (ASTM D 5996)	X	. . .	. . .
Chemically suppressed (ASTM D 5542)	. . .	X	. . .
Electronically suppressed	. . .	X	For high concentrations only

Table 6-3.12   Iron

Method	Usage: On-Line	Usage: Grab	Comments
Bathophenanthroline colorimetric (ASTM D 1068 D)	. . .	X	$\mu g/L$ (ppb) range 40–1,000 $\mu g/L$
Atomic absorption, direct (ASTM D 1068 A)	. . .	X	$\mu g/L$ (ppb) range 100–5,000 $\mu g/L$
Atomic absorption, graphite furnace (ASTM D 1068 C)	. . .	X	$\mu g/L$ (ppb) range 5–100 $\mu g/L$

Table 6-3.14   Organic Anions

Method	Usage: On-Line	Usage: Grab	Comments
Oxidation/CO_2 detection (ASTM D 5173 and D 5997)	X	. . .	TOC
Oxidation/CO_2 detection (ASTM D 6317)	. . .	X	TOC
Ion chromatography (ASTM D 65996)	X	X	. . .

6-3.14 Organic Anions

Anions that may form weak acids that contain carboxylic acid component (–COOH). Organic anions, predominantly formic and acetic, are formed by the decomposition of organic additives, ion exchange, Dl resin, lubricants, and organics in make-up water, which have leaked into the cycle.

Organic anions add to specific and cation conductivity and may be corrosive. Detection by methods other than conductivity is needed to isolate this organic contamination from other sources (see Table 6-3.14).

6-3.15 ORP

Oxidation-reduction (or redox). Potential measurement is used to indicate the relative degree of oxidizing or reducing conditions in water. In cycle chemistry, the water is in equilibrium with the protective iron and/or copper oxide layers of cycle components. ORP is influenced by reducing agents, such as hydrazine and ferrous ions, which drive its value lower, and also by oxidizing agents, such as oxygen and ferric ions, which raise its value. ORP is most useful in monitoring reducing chemistries, whereas dissolved oxygen is more sensitive in monitoring oxygenated treatments. The interpretation of ORP values in cycle chemistry samples is somewhat controversial.

In make-up water treatment, ORP is commonly used to ensure the removal of chlorine or other oxidizing agents ahead of membranes or de-ionization resins that could be damaged by oxidation (see Table 6-3.15).

6-3.16 Oxygen Scavengers

Reducing agents that consume dissolved oxygen. The list below defines most of the known oxygen scavengers (see Table 6-3.16).

  (a) hydrazine
  (b) sodium sulfite
  (c) ferrous sulfate
  (d) sodium bisulfite
  (e) erythorbate
  (f) cabohydrazide
  (g) DEHA (diethyl hydroxylamine)
  (h) DEHA + hydroquinone
  (i) cyclohexylamine erythorbate
  (j) hydroquinone
  (k) hydroquinone + MOPA (methoxypropylamine)
  (l) catalyzed hydroquinone
  (m) methylethyl ketoxime
  (n) morpholine (reacts with O_2 but not considered a scavenger)
  (o) isoascorbate

Table 6-3.15 Oxidation-Reduction Potential (ORP)

Method	Usage: On-Line	Usage: Grab	Comments
Electrometric instrumental probe (ASTM D 1498)	X	X	. . .

Table 6-3.16 Oxygen Scavengers (Reducing Agents)

Method	Usage: On-Line	Usage: Grab	Comments
Vendor-specific instruments	X	X	. . .

Table 6-3.17 pH

Method	Usage: On-Line	Usage: Grab	Comments
Electrometric instrumental probe (ASTM D 1293 and D 5464)	. . .	X	. . .
Electrometric instrumental probe (ASTM D 5128)	X	. . .	. . .

CAUTION: **Some oxygen scavengers have been determined to be a health hazard. Consult supplier for additional information.**

6-3.17 pH

The negative logarithm of the concentration or activity of hydrogen ion. pH provides an indication of the acidic or alkaline tendency of water. It is determined by measuring the potential difference between a pH-measuring electrode and reference electrode immersed in the sample. Both electrodes may be contained in a single probe. The pH meter and electrodes are standardized against two reference buffer standards with values near the anticipated sample pH.

Temperature changes both electrode response and the chemical equilibrium in the sample. The former is routinely compensated automatically. Compensation for changes in chemical equilibrium requires knowledge of the sample temperature coefficient and in many cases can be compensated automatically with appropriate instrumentation and settings.

pH is an important consideration in determining the corrosive action of water and assessing water treatment practices. Corrosion in a boiler is very pH dependent. For example, at low pH (below 9.0) in deaerated solutions, iron corrosion will increase, and at high pH, copper corrosion will increase. The optimum pH level will depend on the particular plant, cycle, materials used, and operating conditions and is usually determined experimentally by observing the levels of corrosion products in the water while the plant operates. In large power plants, pH of the feedwater is usually controlled by the addition of ammonia or other amines between the condensate and boiler feed pumps (see Table 6-3.17).

pH above 8.0 may be estimated from specific conductivity and cation conductivity that are measured at 25°C

or are accurately temperature compensated to 25°C. In general, the method uses a formula of the following form:

$$pH = \log (S - aC) + b$$

where
- a = constant approximately equal to 0.3
- b = constant approximately equal to 8.57
- C = cation conductivity (−S/cm at 25°C)
- S = specific conductivity (−S/cm at 25°C)

This method can give very precise estimates of pH when the specific conductivity is high (>2 μS/cm) and cation conductivity is low (<0.3 μS/cm) but shows considerable error at high cation conductivities and low specific conductivities. Although the method is useful, particularly in feedwater streams with pH above 8.0, it does not completely replace the need for pH electrodes.

6-3.18 Phosphate

Anionic form of phosphoric acid (PO_4^{3-}). Sodium phosphates are used as internal boiler water treatment chemicals to prevent scale buildup on heat transfer surfaces of modern industrial and utility boilers and to provide pH and alkalinity elevation while minimizing availability of hydroxide ions. Phosphates most widely used are disodium and trisodium phosphates, which may be fed individually or in blends. Sodium phosphates (possibly with the addition of NaOH) provide the desired pH in the boiler water and moderate the effects of condenser leakage (see Table 6-3.18).

6-3.19 Reducing Agents

See para. 6-3.16.

Table 6-3.18 Phosphate

Method	Usage: On-Line	Usage: Grab	Comments
Amino reduction colorimetric	. . .	X	. . .
Colorimetric	X	X	. . .
Ion chromatography (ASTM D 4327)	X	X	. . .

Table 6-3.20 Silica

Method	Usage: On-Line	Usage: Grab	Comments
Colorimetric (ASTM D 859)	. . .	X	. . .
Colorimetric	X	. . .	. . .
Atomic absorption, graphite furnace (ASTM D 4517)	. . .	X	Detects total silica. Recommended, especially when significant non-reactive silica is present.

6-3.20 Silica

Silicon is the second most abundant element on earth. It is present in water as silicate anion as well as in colloidal forms. Silica is monitored at a number of locations throughout the steam-water cycle. Generally, silica becomes a concern in the steam cycle as it passes over from the boiler water into the steam as silicic acid, which deposits as silicate on turbine blades as the steam pressure and temperature drop during passage through the turbine. Silica deposits on turbine blades are very difficult to remove, degrade efficiency, and, in extreme cases, can lead to steam turbine failure.

Silica is a very weakly ionized anion and therefore difficult to remove by ion exchange. It is therefore monitored following anion and mixed-bed exchangers in both makeup treatment and condensate polishing (see Table 6-3.20).

6-3.21 Sodium

Alkali metal present in water as cation Na^+. The determination of the sodium content is utilized in the assessment of steam purity, condenser in-leakage, and condensate polisher and makeup demineralizer performance. Its testing and control is critical in steam samples where sodium hydroxide and sodium chloride have been directly linked to turbine failures. Sodium compounds can also lead to boiler and economizer tube failures.

Condensers are a primary source of contamination in the steam-water cycle. Since the condensate is under vacuum, any leakage in the condenser results in cooling water entering the condensate. Cooling water (either fresh water or sea water) contains a relatively high concentration of sodium. With detection capability less than $1~\mu/L$ (ppb), sodium ion analysis provides a very sensitive means to detect condenser leaks.

Ionic impurities entering the steam-water cycle can be removed by condensate polishing demineralizers.

Sodium is usually the first ion to break through upon exhaustion of the cation exchange resin. Sodium-ion measurement is particularly significant in the operation of ammoniated cation resins, since it is the only means of detecting early breakthrough (see Table 6-3.21).

6-3.22 Sulfate

Anionic form of sulfuric acid (SO_4^{2-}). The sulfate ion is an aggressive ion and can cause corrosion. The intrusion of sulfate may result from condenser leaks, condensate polishers, or makeup demineralizers. Cation and specific-conductivity measurements may serve to indicate such mineral contamination, but this measurement doesn't distinguish whether the mineral contamination is chloride, sulfate, other mineral anions, amine, or carbon dioxide (see Table 6-3.22).

6-3.23 Total Organic Carbon (TOC)

Total content of organic-bound carbon present in water. Also see para. 6-3.14. The primary purpose of total organic carbon analysis is to determine fouling tendencies in the raw water supply and/or returned condensate from cogeneration steam users. Monitoring of organics removal in the demineralizer is also possible. Some TOC analyzers also measure CO_2 (see Table 6-3.23).

6-3.24 Trace Metals

See paras. 6-3.7 and 6-3.12. Other trace metals, such as nickel, chromium, zinc, aluminum, and lead, can also be monitored (see para. 6-4.1).

6-3.25 Turbidity

ASTM defines turbidity as "reduction of transparency of a sample due to the presence of particulate matter." Plants using surface-water supply rely on coagulation, settling, and filtration to ensure an acceptable effluent. Turbidity measurements are sometimes made on cycle

Table 6-3.21 Sodium

Method	Usage: On-Line	Usage: Grab	Comments
Ion-selective electrode (ASTM D 2791 A)	X	. . .	. . .
Flame photometry (ASTM D 2791 B)	X	. . .	. . .
Ion chromatography	X	X	. . .
Atomic absorption (ASTM D 4191 and D 3919)	. . .	X	Over 200 µg/L (ppb) range
Flame photometry	. . .	X	. . .

Table 6-3.22 Sulfate

Method	Usage: On-Line	Usage: Grab	Comments
Ion chromatography (ASTM D 5996)	X	. . .	. . .
Ion chromatography (ASTM D 5542)	. . .	X	. . .

Table 6-3.23 Total Organic Carbon (TOC)

Method	Usage: On-Line	Usage: Grab	Comments
Oxidation/CO_2 detection (ASTM D 5173 and D 5997)	X	. . .	. . .
Oxidation/CO_2 detection (ASTM D 6317)	. . .	X	. . .

Table 6-3.25 Turbidity

Method	Usage: On-Line	Usage: Grab	Comments
Nephelometric (ASTM D 6698)	X	. . .	Over 5 NTU

water samples as a qualitative means of monitoring corrosion products. Much of the metal found in the cycle is in the finely divided oxide form. This is especially true during startups when metal concentrations are high. However, turbidity will detect only solid forms of metals and metal oxides described in para. 6-3.1.

Total suspended matter can be estimated by continuous on-line monitoring instruments (turbidimeters and/ or nephelometers) in which light is reflected from the suspended particles. Such instruments permit observation of the changes in the amount of suspended material in the water. They do not differentiate between different contaminants (see Table 6-3.25).

6-4 OTHER METHODS

6-4.1 Sampling of Metals and Metallic Oxides

The presence of metals or metal oxides in condensate and feedwater is undesirable as they become constituents of, and contribute to the formation of, deposits in the steam generator, turbine, and other components of the cycle. Typical of the metals and oxides that are important are iron, copper, nickel, chromium, zinc, lead, and

aluminum. The form in which metal contaminants exist at any point in the cycle is dependent on the temperature and chemical environment. Deposits rich in these materials are found in critical areas of filters, orifices, heater tubes, steam generator tubes, and turbine blades.

Metal oxide deposits on steam generator tubes and feedwater heater tubes can impair heat transfer, increase pressure drop, and may promote corrosion. Deposits in turbines decrease efficiency and capacity and may lead to localized corrosion. Metallic and metal oxide contaminants in condensate or feedwater usually indicate corrosion, erosion, or both in the preboiler system. Significant amounts of these materials may disclose inadequate or improper conditioning of the condensate, feedwater or makeup, incomplete deaeration, postdeaeration inleakage of air, improper handling of heater vents and drips, improper materials selection in critical parts of heaters or condenser, excessive fluid flow velocities in one or more components of the system, or design defects.

Significant increase in metal contaminants can be expected under certain conditions, such as startup or cyclic operation. The suspended and dissolved metallic contaminants in samples do not necessarily exist in the

same ratio or form as in the sampled water. Attempts to differentiate between soluble and suspended contaminants can be misleading. Determination of the total concentration of metal contaminants generally gives the most consistent results, but may not be the best basis for evaluation.

The presence of such material can be detected with membrane filters, through which known quantities of water are passed. The resulting coloration and amount of deposit can be interpreted in terms of suspended matter concentration by comparison with a calibration chart prepared at the sampling site. Temperature affects the color of a deposit, and the calibrations are applicable only when the environment is duplicated. Filter readings have been found very useful in monitoring system cleanliness. Detailed procedures for preparation of standard iron oxide membrane comparison charts, and determining iron oxide and iron concentration in samples, have been published by ASME and ASTM, and standard comparison charts are available commercially. [12–14]

6-4.1.1 Sampling. The sampling technique for metal contaminants is extremely important. An adequate and constant sampling rate should be maintained to minimize fluctuations in contaminant concentrations due to "hang up" in sample lines and coolers. Samples should be allowed to flow continuously for at least 1 hr (preferably 24 hr) before sample collection for analysis is begun. A new sample line and cooler should be "seasoned" for several hours (preferably several weeks) by continuous sample flow before a sample is taken for analysis. The flow rate of the sample should be 5 ft/sec to 7 ft/sec (1.5 m/s to 2.1 m/s). Refer to Sections 2 through 4 of this Code and ASTM D 6301 for sampling protocol. Refer to ASTM D 4453 for Handling Ultrapure Water Samples. Refer also to ASTM D 4309, Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water, for sample preparation for analysis by AA or Inductively Coupled Plasma (ICP).

6-4.1.2 Summary of Methods for Metals Using Grab Samples. The method of choice for the analysis of metals in grab samples is atomic absorption (ASTM D 3919 and D 4691). However, this instrument may not always be available.

Photometric methods are suitable alternatives but are more labor-intensive. The information below can be used as a guide by the analyst. If available, ICP Spectroscopy (ASTM D 1976, D 4190, and D 5673) is an excellent technique for determining multiple elements simultaneously in a single sample.

NOTE: Some of these methods have produced lower levels of detection than claimed.

6-4.1.2.1 Iron. Refer to ASTM D 1068.

Method	Range
A - Atomic absorption, direct	100–5,000 μg/L
C - Atomic absorption, graphite furnace	5–100 μg/L
D - Photometric bathophenanthroline	40–1,000 μg/L

6-4.1.2.2 Copper. Refer to ASTM D 1688.

Method	Range
A - Atomic absorption, direct	50–5,000 μg/L
B - Atomic absorption, chelation-extraction	50–500 μg/L
C - Atomic absorption, graphite furnace	5–100 μg/L

6-4.1.2.3 Nickel. Refer to ASTM D 1886.

Method	Range
A - Atomic absorption, direct	100–10,000 μg/L
B - Atomic absorption, chelation-extraction	10–1,000 μg/L
C - Atomic absorption, graphite furnace	5–100 μg/L

6-4.1.2.4 Chromium. Refer to ASTM D 1687.

Method	Range
A - Photometric diphenylcarbohydrazide	10–500 μg/L
B - Atomic absorption, direct	100–10,000 μg/L
C - Atomic absorption, graphite furnace	5–100 μg/L

6-4.1.2.5 Zinc. Refer to ASTM D 1691.

Method	Range
A - Atomic absorption, direct	50–2,000 μg/L
B - Atomic absorption, chelation-extraction	20–200 μg/L

6-4.1.2.6 Aluminum. Refer to ASTM D 857.

Method	Range
Atomic absorption, direct	500–5,000 μg/L

6-4.1.2.7 Lead. Refer to ASTM D 3559.

Method	Range
A - Atomic absorption, direct	1,000–10,000 μg/L
B - Atomic absorption, chelation-extraction	100–1,000 μg/L
C - Differential pulse anodic stripping voltammetry	1–100 μg/L
D - Atomic absorption, graphite furnace	5–100 μg/L

6-4.1.2.8 All Metals. Refer to ASTM D 6502 and D 2332. Membrane filters and cation resin membranes described in subsection 6-4.1.3 are also analyzed nondestructively by X-ray fluorescence for a wide range of metals. [16-20]

It is important that the analyst carefully reviews the method chosen to ensure that it is applicable to the sample. Considerations are: expected concentration of the metal, quantity of sample available, oxidation state, interference expected to be present, availability of required instrumentation, and proper preparation of the sample for analysis.

6-4.1.3 Integrated Sampling for Corrosion Products.

Integrated sampling procedures or sample preconcentration may be necessary to obtain reasonable estimates of corrosion products in some feedwater systems. [15-20]

A commonly used approach used during startups and with cycling plants is to obtain 1 L to 4 L of sample from a continuously flowing sample stream and filter the sample in the laboratory through a 0.45-μm membrane filter. Preferably, three cation resin-impregnated membranes should be inserted below the membrane filter to collect soluble and colloidal species.

Where long-term operation is to be monitored, a similar technique can be used on-line. A 0.45-μm membrane filter followed by three cation resin-impregnated membranes are used to collect the metal oxides. A continuous sample flow rate of 50 mL/min to 100 mL/min and sampling periods of several hours to 7 days have been used.

The on-line integrated collection method allows long-term averaging of corrosion product concentrations. Mass balances can be performed around major components, and major sources of the corrosion products within the feedwater system can be identified.

NOTE: Sample streams feeding this apparatus and other analysis should be isokinetically split to ensure that the corrosion products are properly represented in the sample.

The deposits on the membrane filters can be dissolved and the cations regenerated from the cation resin membranes. The resultant solutions are analyzed by atomic absorption or the photometric methods described above. Membrane filters and cation resin membranes are also analyzed nondestructively by x-ray fluorescence for a wide range of metals.

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Section 7
Data Acquisition and Data Analysis

7-1 INTRODUCTION

Techniques for data acquisition and storage change rapidly. Section 7 is to give very general guidance why data storage is needed and what to consider when storing data.

7-2 PURPOSE OF DATA AND DATA STORAGE

The processes of data acquisition and data analysis are defined by the intended use of the data. Data are collected for a number of purposes. The purposes set the requirements on the data. Typical uses include trending and day-to-day control, warranty issues, and root cause analysis.

7-2.1 Trending and Day-to-Day Control

The first use of most chemistry data will be control of cycle chemistry. Many of these systems will have feedback loops for which the time delays in the sample lines can be important. The daily control also requires annunciation of chemical upsets. Setting alarms appropriately can be an art. Generally, one wants to keep alarms near the point where timely action is required.

7-2.2 Warranty

Many contracts require that chemistry data be collected and conform to specified requirements in order to maintain the warranty. The quality and quantity of the data can be important to the successful prosecution of a warranty claim.

7-2.3 Root Cause Analysis

Root cause analysis, typically in support of corrosion or deposition problems, is often the most demanding use of the data. It will quickly reveal the flaws in the data storage. Much of the discussion in this Section will be in support of root cause analysis.

7-3 DATA QUALITY

Unless the data are of high quality, there is little value in storing them. Data quality consists of accuracy, precision, and reliability. Section 6 has information on limits to data accuracy and precision. Vendor literature also has such information.

7-3.1 Calibration and Validation

7-3.1.1 Calibration. Instrument calibration is necessary to quality data. While auto-calibration features can

make this problem smaller, it does not entirely eliminate it. Vendor calibration frequencies should be respected.

7-3.1.2 Validation. Validation consists of comparison with similar data, consistency checks, required relationships, QA/QC, and statistical analysis. Validation shows that monitors are giving accurate and reliable data.

7-3.1.3 Annotation of Out-of-Spec Data. Automated data collection systems store all data, whether they are correct or not. It is important to be able to state whether the data are valid or not, and this should be done while or shortly after the data are collected. Digital signals that alert the Digital Control System (DCS) that an instrument is in calibration are an example of data annotation. Logs kept in a well-known place are another example. All out-of-specification data should be annotated. It may be a real process excursion, an out-of-service instrument, an instrument in calibration, bad sample flow, or any of a number of other reasons. These annotations prevent people reviewing data, perhaps years after the data were collected, from drawing erroneous conclusions or ignoring all the data because an excessive fraction is clearly bad data.

7-3.1.4 Instruments on Several Samples. When several sample streams may be analyzed by the same instrument, it is important to note which sample is feeding the instrument. This is a most significant problem when the data are archived in an electronic historian. The simplest notation is a log book. If that is readily accessible when the data are analyzed, it may be adequate. Even better are systems that indicate to the electronic recorder which sample point is being analyzed.

7-4 DATA STORAGE ISSUES

Storage requirements are based on the intended future use of the data. As previously noted, the most demanding use is for root cause analysis of corrosion or deposition problems. That use will generally define the responses to the rest of this Section. A second use is for assessing exposure to chemicals and can be viewed as the recording of ppb-hours of a particular species.

7-4.1 Complementary Data Needs

Chemistry data need to be supplemented with enough general plant data to determine what is happening in the plant at a given time. Examples include load and

turbine speed, condensate pump outlet pressure, and the like. Most of these parameters will be commonly stored in data historians, but one must be sure to request them for analysis.

7-4.2 Recording Frequency

Recording more than once per minute is rarely important for chemistry data from continuous analyzers since the instrument time constants tend to be on the order of 1 min and the changes slower than that. Recording continuous analyses once per 5 min may lose information. When the analysis is a batch analysis, the recording frequency is defined by the frequency of the analysis.

7-4.3 Compression

Various compression techniques have different advantages and disadvantages. Time averaging reduces storage by a known factor but tends to lose the information in the extreme data. Dead-banding is the storing of a datum and time only when the change has exceeded a particular quantity. Dead-banding reproduces excursions more accurately but does not give a specific reduction in storage requirement. The user must select a technique appropriate to the end use of the data as defined in subsection 7-2.

7-4.4 Retention Time

The retention time is determined by the end use of the data. Daily trending requires little long-term storage.

Warranties require storage only until the warranty issues have expired. Root cause analysis may need to go back to the initial installation of the equipment and the commissioning period and is likely the concern that defines retention time.

7-4.5 Archives for Nonelectronic Data

Nonelectronic data can be a significant part of the total chemistry data. Examples include records of grab sample analyses, condenser leakage, condensate polisher regenerations, air in-leakage determinations, etc.

7-4.5.1 Logs. Logs can be an effective means of storing the nonelectronic data. The logs can be either electronic or paper. Such logs will not necessarily be well integrated with the electronic data, but such integration will be critical to good data analysis.

7-4.5.2 Physical Archives. It is also important to store certain physical specimens, such as corrosion product filters used for iron analysis during startups, and boiler tube samples taken for deposit analysis.

7-4.6 Retrievability and Searchability

As the quantity of data increases, it is important to be able to know what data are available and how to find it. Storage methods should be minimally platform dependent. Good computer directory architecture is important. Databases of available data are also helpful. Appropriate backup is essential.

Nonmandatory Appendix A
Leakage Detection and Measurement

A-1 INTRODUCTION

A-1.1 General

This Nonmandatory Appendix specifies methods and apparatuses for detecting, locating, and measuring leaks into the power cycle. The leaks of primary concern are contaminants from the cooling water cycle into the condensate cycle and of air into the condensate and feedwater cycle. Other leaks, such as boiler tube leaks and heater leaks that may affect test results, are also addressed. The term "leakage" as used in this Nonmandatory Appendix is defined as the material that escapes its normal, confining barrier.

Leakage of cooling water and air in-leakage into the steam space of the condenser must be at or less than the maximum permissible level specified in the governing Performance Test Code, before a performance test of a turbine and condenser is conducted. In general, a condensate or feedwater flow measurement test is not started until the parties agree that the leakage is within acceptable limits. After initial construction or rework of the condenser, the cold water hydrostatic pressure test is the most commonly used off-line method to detect potential condenser cooling water leaks and condenser air in-leakage. Dyes are often used with this method.

Load changes may cause temporary false indications of condenser leakage, since changing load may cause a washing of deposited material from the turbine and heaters, which in turn will affect physical and chemical ion measurements.

Although specific safety concerns are not within the scope of this Code, the reader should address all safety concerns whether dealing with the mechanical equipment or chemicals in applying any procedures referenced.

A-1.2 Cooling Water Leaks

The primary methods for detecting cooling water leaks into the steam space, while the condenser is in service, include cation conductivity, selective ion analyzers, and tracer techniques.

Methods for locating the cooling water leaks include dyes, tracers, plastic films, flexible diaphragms, soap bubbles, eddy currents, sonic pulses, and ultrasonic techniques. The ultrasonic technique requires a unit outage.

A-1.3 Air In-Leakage

The most direct method for detecting air in-leakage is monitoring the flow measurement devices on the air ejectors or pump discharges. In addition, monitoring performance parameters, such as condenser pressure, hot well oxygen concentration, and subcooling, will aid in identifying excessive air in-leakage.

Methods for locating air in-leakages include ultrasonic testing, infrared imaging thermography, and tracer testing, in addition to the hydrostatic pressure test. Use of the tracer method of helium has increased significantly because of its increased sensitivity and effectiveness in locating leaks.

A-1.4 Test Results

Leakage into or out of the power cycle will affect test results. Cooling water leakage measurements can be used to correct observed and calculated test data. However, the leakage data must be obtained with accuracy equivalent to the accuracy of the test data.

A-2 COOLING WATER IN-LEAKAGE

A-2.1 General

Cooling water in-leakage can quickly cause a power-generating station to be forced into a reduced load condition necessary for the application of condenser leak detection techniques. In the worst case, the station can be forced into an immediate shutdown to prevent the formation of scale and/or corrosion in systems. When a condenser leak occurs that affects plant performance, it is of highest priority to find and correct the leak in the shortest possible time The choice of leak detection methods depends on the size of the leak and type of instrumentation that is available. With a large leak, such as a cracked or broken condenser tube, simple methods can rapidly locate the failure. Small leaks that seep and change their leakage rate with load cycles require precise application of sensitive methods. Condenser design also affects how samples to detect in-leakage should be taken. The condenser manufacturer should be consulted for recommended sampling locations.

The following summarizes methods that are in common use:

(a) on-line
  (1) cation and degassed cation conductivity
  (2) selective ion sodium analysis
(b) Differential pressure methods (vacuum)
  (1) sonic detection
  (2) plastic film
  (3) foam testing