The International Association for the Properties of Water and Steam

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Technical Guidance Document – 2012 Revision: Instrumentation for monitoring and control of cycle chemistry for the steam-water circuits of fossil-fired and combined-cycle power plants

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This technical guidance document was first issued in 2009. In response to comments received, this revision includes a small number of minor updates and clarifications. These do not constitute significant changes to scope of the document or to the guidance contained.

In order to achieve suitable chemical conditions in steam/water circuits, it is essential to establish reliable monitoring of key parameters on every plant. This enables the demonstration of operation within cycle chemistry targets, and alerts the operators to the need to take corrective action when the target conditions are compromised.

This technical guidance document considers conventional fossil and combined-cycle/HRSG plants and identifies the key instrumentation and monitoring techniques required for each plant type and cycle chemistry treatment. It is emphasized that this is an IAPWS guidance document and that, depending on local requirements, the use of simpler instrumentation may be adequate, whereas more complex techniques and instrumentation may be necessary when specific issues arise.

Further information about this guidance document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from http://www.iapws.org.

Contents

1. Nomenclature and Definitions

Term	**Alternative or Acronym**	**Definition**
All-volatile Treatment	AVT AVT(R) AVT(O)	Conditioning regime in which only volatile alkalising agents are used (commonly ammonia – volatile amines may also be employed). May be either: Reducing conditions (added reducing agent) or Oxidizing conditions (residual oxygen present)
Attemporator		Device for controlling superheater and reheater outlet temperatures by spraying feedwater (or condensate or degassed demineralized water) into steam.
Caustic Treatment	CT	Conditioning regime for drum boilers in which alkalinity is achieved by dosing with NaOH.
Condensate		Water that derives from condensation of steam after passage through a steam turbine or process heat exchanger.
Conductivity	Specific Conductivity Direct Conductivity	Electrical conductivity of an unmodified water sample.[1]
Conductivity after cation exchange	Cation Conductivity Acid Conductivity CACE	Conductivity of a water sample after passage through a strongly acidic cation exchanger in the hydrogen form.
Degassed conductivity after cation exchange	Degassed Cation Conductivity	Conductivity after cation exchange of a sample from which volatile weak acids (predominantly carbonic acid) have been stripped.
Drum boiler		Boiler in which steam (generated in heated evaporator tubes) is separated from water in an unheated horizontal pressure vessel. The liquid phase is recirculated to the evaporator.
Feedwater		Water that is being pumped into a boiler or HRSG to balance the steam production.
Heat Recovery Steam Generator	HRSG	Plant that generates steam using heat from the exhaust gas of a combustion (gas) turbine.
Make-up Water		Water which is added to compensate for losses of water and steam from the system.

Term	**Alternative or Acronym**	**Definition**
Once-through boiler or HRSG		Boiler in which output steam is generated from input water by evaporation to dryness without recirculation.
Oxidation/Reduction Potential	ORP	Electrochemical potential of an inert electrode responding to the concentrations of oxidizing and reducing agents in a water sample.
Oxygenated Treatment	OT or CWT	Conditioning regime in which alkalizing agents and oxygen are added. (OT = oxygenated treatment, CWT = combined water treatment)
Phosphate Treatment	PT	Conditioning regime for drum boilers in which alkalinity is achieved by dosing a sodium phosphate compound or blend of compounds.
Total Organic Carbon	TOC	Concentration in aqueous solution of the carbon present in organic molecules and ions. (Excludes carbon present in carbonates, bicarbonates and other inorganic species.)

2. Introduction

Safe, reliable operation of large steam raising and power generating plants depends upon the establishment of chemical conditions throughout the steam-water circuit that minimize the corrosion of constructional materials and suppress the formation of deposits. The chosen chemical treatments and instrumentation will depend upon the details of plant type, circuit design, metallurgy, physical parameters (temperatures, pressures, heat fluxes, etc.) and intended operational mode of the plant (base, medium or peak load operation). In all cases it is essential to be able to measure the key chemical parameters and to take action on the basis of these measurements to ensure that chemical targets are achieved.

This technical guidance document considers conventional fossil and combined cycle/HRSG plants and identifies the key instrumentation and monitoring techniques required for each plant type and cycle chemistry treatment. Thus, for all systems there is a **Minimum Key Level of Instrumentation**. The document also considers **Optional Additional Instruments**, not essential for all plants, but which may provide further useful information to plant operators.

It is important that the operators of a plant consider the following items in developing a Minimum Key Level of Instrumentation:

1. Every plant should have a minimum level of instrumentation which can uniquely identify the key parameters and drivers to each and every failure/damage mechanism which can occur in that plant. In other words the instruments should relate to providing reliability and not necessarily to only chemistry monitoring of individual locations/parameters around the cycle.

2. The Minimum Key Level of Instruments does not necessarily only analyze the chemistry locally, but needs to provide sensitivity analysis for the cycle in the event of a defective or out of service instrument. Thus an instrument within the minimum key level is backed up by instrumentation on either side of the specific instrument so that in the event of a serious contamination the operator does not need to waste time validating the reading of an individual instrument.

3. The Minimum Key Level of Instruments should provide complete assurance to an operator without that operator or his team having to go into the plant to "check" an instrument or to take a grab sample. This relates to point 2.

4. The Minimum Key Level of Instruments should all be audibly alarmed in the control room or on the distributed control system.

Chemical instrumentation can be divided into two categories:

On-line instruments: These give a continuous record of conditions and can be used to provide alarm signals to stimulate operator intervention if the parameters that they are measuring fall outside a pre-defined target range. In some instances the output from such instrumentation may be used in automatic control applications. Information from the key on-line instruments should be provided to the plant data system to enable direct control of operational chemistry, and prompt and appropriate action by the operating staff. Sampling system design is to be the topic of a future IAPWS guidance document. Data from on-line instruments can only be valid provided the flow of sample to the instrument remains within the required range. Data collection systems must be designed to give positive validation of this condition.

Off-line analytical techniques (grab samples): Batch or grab samples are collected at predetermined intervals for analysis. The intervals may vary according to the importance and urgency of action required on the basis of the results. The measurements performed off-line may provide confirmation of the validity of on-line results, and may provide additional diagnostic information when key targets are compromised, but they should not provide the key data on which the plant operation is based.

Provision of the Minimum Key Level of Instruments should minimize the perceived requirement to conduct extensive off-line sampling except in the case of deviation from chemistry targets.

3. On-line Monitoring Techniques

3.1 Key Instruments

All of the on-line monitoring techniques covered in this section contribute to the matrix of **Minimum Key Instruments** which every plant requires for adequate control of the cycle chemistry. The list is not exclusive of other techniques which may prove valuable in some instances but are not universally essential.

3.1.1 Conductivity (or specific conductivity or direct conductivity)

The conductivity of a dilute aqueous solution such as feedwater, boiler/evaporator water or condensed steam provides an immediate indication of the amount of ionic solutes that are present. It is a non-specific technique, giving the charge carrying capacity of all of the cations and anions that are present. The individual ionic conductivities of all of the common ions are known, and for solutions in which a small number of ions dominate, the conductivity can be correlated with their concentration.

Whenever a fault condition leads to a change in the levels of ionic contamination in a sample there is a resulting change in the conductivity. The technique thus provides a robust, simple but non-specific indicator of the onset of such a fault (e.g., contamination via a condenser leak).

For boiler feedwater, steam and condensate the dominant ions contributing to the conductivity are likely to be ammonium (or an amine in some plants) and hydroxide. In the absence of other contaminants the measured conductivity can be directly correlated with ammonia (or amine) concentration.

For boiler/evaporator water (in drum-type boilers, HRSGs and once-through boilers in recirculation mode with low-load conditions) where minor impurities can accumulate, and further chemical dosing may be applied, the correlation of conductivity with solution composition is subject to more variability. However, the measurement remains valuable for rapid determination of trends in chemical conditions within the boiler/evaporator.

The conductivity of ionic solutions varies with temperature. Ionic mobilities are themselves temperature dependent and, when weak bases (such as ammonia and amines) are present, there is an additional influence of temperature on their dissociation. Commercial instrumentation may compensate for deviation from a reference temperature (normally 25 ºC) to variable degrees of accuracy. However, to minimize errors arising from the differing temperature dependencies of conductivities of the various species that may be present, it is beneficial to adjust the sample temperature to be as close to the reference temperature as practicable.

3.1.2 Conductivity after cation exchange (or Cation conductivity or Acid conductivity)

The online measurement of conductivity after water has passed through a column of strongly acidic cation-exchange resin is used to indicate the presence of potentially corrosive ionic contaminants. The technique may be referred to as “cation conductivity” or “acid conductivity” in some documentation.

The cation-exchange resin removes ammonium, sodium, and other cations—leaving an acidic solution of the anions that were present. The conductivity of this solution is highly responsive to the presence of strong-acid anions, because of the very high equivalent conductivity of the hydrogen ion. Thus, conductivity after cation exchange is extremely effective for rapidly indicating the onset of condenser leakage, particularly at seawater-cooled sites, and also for detecting contaminated makeup water.

The technique is most frequently applied to the monitoring of condensate, feedwater and condensed steam. It is also applicable to the monitoring of boiler/evaporator water provided the boiler/HRSG is operating with an All-volatile Treatment or a Caustic Dosing regime.

It can also be used, despite being less directly applicable, for boiler/HRSG evaporator water monitoring in phosphate dosed plant; in this case the dominant contribution of phosphate ions masks any response arising from contaminant species. Irrespective of the effect of the phosphate ions, it is approximately 3.5 times more sensitive than the direct conductivity measurement to the presence of contaminants such as chloride. However, complete interpretation of the data requires independent knowledge of the phosphate ion concentration.

It is common practice to use ion exchange columns filled with a cation exchange resin that changes color as it is exhausted. A color change front propagates along the column in service, enabling the operator to judge when replacement by regenerated resin is necessary. The column may be oriented for downwards or upwards flow; the latter can have advantages in flexibly operated plants where there may be a risk of regular flow interruption.

Conductivity after cation exchange is also responsive to the presence of anions of weak acids, but is subject to the suppression of their effect if the concentration of strong acid anions is sufficient to cause association of the weak acids. An important case is the response to carbonate and bicarbonate from CO_2 contamination of the steam-water circuit. It can be useful to make a measurement of “degassed conductivity after cation exchange” (see Additional Instrumentation) in circumstances where it is necessary to distinguish the presence of potentially more corrosive species in the presence of persistent CO_2 contamination.

3.1.3 pH

The pH of a solution is a key parameter in the control of circuit chemistry. The online measurement is made potentiometrically using a pH-sensitive glass membrane electrode and a nominally pH-independent reference electrode. The ISO Standard 105234:2008 “Water quality – determination of pH” applies [2]. The low ionic content of most power plant samples introduce the following specific considerations:

Adsorption of materials onto the surface of the glass electrode or precipitation in the ground glass diaphragm of the reference electrode can cause some errors. More commonly, problems develop because the reference electrode develops some pH dependency which influences the measured potential difference between the electrodes. These errors arise because the reference electrode operates in a relatively concentrated (in some cases even a saturated) solution of potassium chloride, which is in contact with the much more dilute sample water via a porous ground glass diaphragm. Potassium chloride is chosen because it minimizes the liquid-junction potential across the diaphragm. However the concentration difference is such that osmosis can cause entry of the sample water into the ground glass diaphragm. Sample solutions with an alkaline pH, such as feedwater and boiler water, can generate significant pH-dependent liquid-junction potentials across the diaphragm, causing a reduction in the measured potential difference between electrodes.

Particular problems arise in the measurement of pH in low conductivity water. pH meters are calibrated against buffer solutions with appreciably higher concentration than feedwater or boiler water samples. The liquid junction effects may be appreciably smaller when the standardizing solutions are in use. The result can be pH readings for feedwater, etc. that are persistently low—often by as much as 0.2 or 0.3 on the pH scale.

Modern high quality instruments address this problem by incorporating measures to minimize the liquid-junction potential. Reference electrodes with external reservoirs for the reference solution are used to suppress ingress of the sample water into the ground glass diaphragm. The use of a much more dilute reference solution reduces the osmotic effect. With very careful attention it is possible to reduce errors in pH measurement of feedwater and boiler water to less than 0.05; a more practicable target is to measure pH to within 0.1 on the pH scale. Regular recalibration, at intervals of no greater than one month, is required to achieve this.

pH of water is dependent on temperature. In alkaline solutions the variability of the dissociation constant of water with temperature must be taken into account. Although commercial pH meters may include temperature compensation facilities, these are based on the temperature dependence of the standard solutions, which are used during calibration. The pH of feedwater, boiler water and steam will have temperature dependencies that are different from these standard solutions. The errors arising from these effects are minimized if the sample temperature is adjusted to be as close to the reference temperature (normally 25 ºC) as practicable.

An alternative on-line instrument for the measurement of pH in waters dosed only with ammonia and/or sodium hydroxide relies on a calculation from measurements of the conductivity and the conductivity after cation exchange. This method provides an accurate stable and reliable measurement of pH provided it is used within the range of solution compositions recommended by the instrumentation supplier. Generally this implies use within the pH range 8.0 to 11.5 and not when contaminant levels exceed the concentration of the alkalising reagent. During periods of severe deviation from normal chemistry, the potentiometric methods of pH measurement covered above remain accurate whereas the conductimetric method may introduce significant errors.

3.1.4 Dissolved Oxygen

Targets are set for dissolved oxygen concentrations in feedwater for two main reasons. High concentrations of oxygen, when combined with ionic contaminants (particularly chlorides) can yield a risk of acidic corrosion, which can lead to sudden large scale tube failures in carbon steel evaporators (in high-pressure boiler waterwalls and HRSG high-pressure evaporators). Very low concentrations of oxygen can enable the development of enhanced iron transport and flow-accelerated corrosion in feedwater and in boiler water where all-volatile treatment, AVT, is practiced. Thus reliable measurement of dissolved oxygen is an essential requirement.

Most on-line dissolved oxygen measuring instruments are membrane polarographs; they detect current due to oxygen reduction after the passage of dissolved oxygen through a suitable membrane. These may require skilled maintenance at regular intervals (replacement of membranes, attention to the condition of electrodes and replacement of internal electrolytes) but given the appropriate level of care, they can provide a reliable indication of the dissolved oxygen concentration in the water emerging from the sample line.

There may, in some instances, be a significant risk of errors in dissolved oxygen measurements derived not from the instruments themselves but from reactions taking place in the sample lines. Any residual reducing agents (oxygen scavengers) or organic breakdown products, etc. may cause reduction of oxygen within the sampling line, resulting in an erroneously low measured value. In changing redox conditions, the walls of the sample line may themselves exhibit some oxygen demand. These difficulties may be minimized by cooling the sample as quickly as practicable (i.e., locating a cooler as close to the sample point as possible), by minimizing sample line length and by ensuring that sample flow rate is properly maintained.

3.1.5 Sodium

The on-line measurement of sodium ion provides a very sensitive indication of ingress of contaminants to condensate in plants with seawater-cooled condensers and also of the carryover of dosing solutes from boiler drums into steam. Glass electrodes, sensitive to the presence of sodium ions, are used at controlled high pH (achieved by the dosing of ammonia or a suitable amine into the sample flow). These are capable of giving reliable measurements down to concentrations of $\sim 0.1\ \mu g \cdot kg^{-1}$.

The sensitivity of sodium electrodes may tend to reduce if they are persistently exposed to very high purity water with very low sodium content. Therefore the instrumentation maintenance schedule must include calibration at regular intervals. The calibration solutions serve to maintain the responsiveness of the electrode as well as providing an indication of any deterioration.

3.1.6 Phosphate (only for those drum boilers where a phosphate dosing regime is applied)

The on-line analysis of phosphate using a dedicated instrument requires a higher level of operator care than many of the other key techniques. A colorimetric technique is used in which the sample is mixed with an acidic solution containing ammonium molybdate together with a redox controlling reagent. In the presence of phosphate a blue compound is generated and its concentration is detected spectro-photometrically.

The phosphate monitor contains a stock of reagents which must be replenished at regular intervals and may have a peristaltic pump which, from time to time, requires maintenance. Thus, appropriate maintenance schedules are essential for reliable operation of these instruments.

At plants where, for other purposes, regular analyses of boiler water by appropriate chemical techniques, for example ion chromatography, are undertaken, the use of on line phosphate monitors may not be considered essential.

3.1.7 Oxidation/Reduction Potential (ORP)

The redox condition of feedwater can provide information that is particularly valuable to operators of plants with copper alloys present in the condenser and/or feed circuit. Such plants require reducing feedwater chemistry for optimum operation and this is readily confirmed by ORP measurement. (Note that this technique is only included in the Key Instrumentation set for this group of plants and not for units which have no copper alloys in contact with feedwater.)

The instrument simply measures the electrode potential of an inert surface (generally platinum) against a reference electrode. The measured potential becomes more positive as the balance of species present in the water becomes more oxidizing. Copper alloys in the feedwater corrode at a greater rate and copper (as ions and/or oxide particles) can be released into the circuit when oxidizing conditions exist. Thus the measurement is used to alert operators to the need to address issues such as air ingress, deficiency in dosing of reducing agents, etc.

3.2 Optional Additional on-line Instruments

In addition to the **Minimum Key Instruments** discussed above, there are a number of **Additional Instruments** which may be deployed with advantage at many plants. The choice of whether to use additional instruments will depend upon factors such as vulnerability of the plant to specific problems such as air ingress, organic contamination of make-up water, presence of silicaceous contaminants in make-up water, etc. Consideration must also be given to the maintenance and calibration requirements to ensure reliability of the data from the additional instruments.

3.2.1 Degassed conductivity after cation exchange (Degassed cation conductivity)

Instrumentation may be used that enables the measurement of conductivity after cation exchange after the most volatile weak acids (particularly carbonic acid) have been removed from solution (generally by boiling or by equilibration with a gas stream). This is most useful for determining the condition of steam (from a condensed sample) since it can be related to the purity criterion for operation of a condensing steam turbine. Particular care is required with temperature compensation or cooling to the reference temperature (25 ºC). Also the efficiency of removal of volatile weak acids can vary according to details of the technique used.

The technique is not classified within the Key Instrumentation group because it is not required in units that are free of excessive weak acid contamination. Thus its use is only justified in particularly vulnerable plants.

3.2.2 Silica

Targets may be set for silica in drum boilers providing steam to turbines in order to ensure that the risk of deposition within the turbine is adequately controlled. Since the essential requirement is to meet a target in the steam, it is generally more directly appropriate to measure the silica content of the steam (or in feedwater for once-through boilers). The technique is not classified within the Key Instrumentation group for all plants because units that have been demonstrated to be free of persistent silica contamination may be operated without continuous confirmation of this state (i.e., a limited program of batch analysis may suffice for such plants). The level of maintenance required for on-line silica analyzers is such that it is only justified in particularly vulnerable plants. In such plants, it is preferable to identify the route of silica ingress (frequently the outlet of the make-up water treatment plant) and to monitor this point in order to enable appropriate action to be taken.

Note that some silica in make-up water may be present in non-reactive form. This has implications for analysis and can hinder the identification of the source of the contaminant. Hydrolysis of non-reactive silica at higher temperatures can then yield reactive silica in boiler water and steam.

The measurement of silica uses a colorimetric technique in which the sample is mixed with ammonium molybdate at a controlled low pH to generate a blue compound that can be detected spectro-photometrically.

Silica analyzers may be deployed as multichannel instruments, with the possibility to switch between multiple samples.

Appropriate maintenance schedules are required to ensure replenishment of reagents, to check operation of pumping and mixing systems, and to recalibrate.

3.2.3 Total Organic Carbon

The presence of organic materials in make-up water can have a detrimental influence on make-up water treatment plant operation. Some organic materials reaching the steam water circuit may cause the formation of deposits that impact on heat transfer and may generate potentially corrosive degradation products.

Measurement of general levels of organic contaminants is achieved by oxidation to carbon dioxide. The total organic carbon, TOC, is then quantified from the resultant increase in carbon dioxide. The technique is non-specific, providing no definitive information on the nature or source of the organic materials present.

4. Circuit Locations for On-line Monitoring

This document covers the requirements for monitoring of a wide range of steam/water circuits of generating and equivalent plants. The range includes drum and subcritical and supercritical once-through boilers in conventional fossil-fired plants together with the heat recovery steam generators of combined cycle plants. In combined cycles, the inclusion of multiple pressure circuits, will, in some cases introduce complexities, particularly where low pressure systems operate, in part, as feed circuits for higher-pressure systems. The scope of coverage also includes some cogeneration plants in which part or all of the condensate may derive from steam used in an application that is external to the main circuit. This can introduce additional requirements for monitoring.

In all cases, it is essential to ensure adequacy and reliability of sample extraction, conditioning and delivery to the instruments. Full discussion of this vital requirement will be covered in a separate guidance document.

It is emphasized again that this is an IAPWS Technical Guidance Document and that, depending on the requirements, the use of simpler instrumentation may be adequate, or even more complex techniques and instrumentation may be necessary when specific issues arise. Wherever practicable, the results from such sources should be used to guide longer term actions, leaving adequate time for the validation of data.

4.1 Make-up Water

All steam generating circuits require a source of make-up water to balance losses via boiler blowdown systems, etc. The make-up water flow will, in most circuits, be a small proportion of the steam generation rate, but in some co-generation applications it may be much larger (up to 100% in cases of zero returned condensate). In the latter cases there may be additional requirements for monitoring to confirm purity.

The purity of make-up water is critical. It is necessary to consider both newly purified water at the make-up water treatment plant outlet and stored condensate which may contain some dosed ammonia or amine and, potentially, some undesirable contaminants.

> For demineralized water the **Minimum Key Level** requirement is measurement of **conductivity** upstream of the point of mixing with dosed condensate.
>
> For condensate from a storage tank open to atmosphere (vented) the **Minimum Key Level** requirement is measurement of **conductivity after cation exchange** upstream of the point of delivery of the water into the main circuit.

For units with a history of silica accumulation, the deployment of a **silica** monitor will be justified (note the comments on non-reactive silica in section 3.2.2).

For units with a history of organic contamination of make-up water, the measurement of total organic carbon, **TOC**, may be justified.

4.2 Condensate

Monitoring of condensate (usually at the condensate extraction pump discharge, CPD) is essential in all plants to provide the first warning of ingress of contaminants as a result of condenser leakage, regenerant chemicals from the makeup plant, or contaminated condensate from a storage system. This location also provides an indication of air in-leakage. The point of measurement is normally the CPD because of the requirement for pressure in the sample line to be greater than atmospheric pressure.

The following instruments should be included in the **Minimum Key Level** at the CPD:

Conductivity after cation exchange is the most important parameter at this point because it rapidly alerts the operator to ingress of potentially corrosive anions.

Sodium measurement is particularly valuable in plants cooled by saline waters, particularly if there is a high risk of condenser leakage and there is no provision for condensate polishing. It offers higher sensitivity than conductivity after cation exchange provides. Consequently, the smallest leaks identified may be extremely difficult to locate and eliminate but their escalation is most readily monitored by sodium measurement. (Optional, but strongly recommended, for plants on freshwater-cooled sites and not necessary for plants with air-cooled condensers).

Dissolved oxygen measurement provides a valuable indication of air ingress rate and of oxygen entering into the high pressure part of the cycle.

The following **Optional Additional Instruments** may be included at the CPD:

Conductivity and **pH** are not always measured, but can provide useful confirmatory information.

In plants that are vulnerable to high air ingress rates or to the presence of carbonate as a result of oxidation of organic impurities, the measurement of **degassed conductivity after cation exchange** can provide useful additional information.

4.3 Feedwater

In conventional plants, feedwater composition is normally monitored at the economizer inlet, EI. This point is downstream of the low-pressure feed heaters, deaerator and high-pressure feed heaters. Combined cycle plants do not have all of these feed heaters and the appropriate sampling points will usually be downstream of the feed pumps; however, in some more modern plants a sampling location upstream of the pumps is chosen to reduce the pressure-related safety requirements. For those low pressure circuits where the drum operates at pressure derived from the condensate extraction pump, the sample from the CPD is appropriate.

For units with condensate polishing systems, it is necessary to provide additional dedicated monitoring at the condensate polisher outlet, CPO. Careful consideration of the circuit configuration is necessary, particularly when there are multiple parallel paths, in order to ensure that the instrumentation warns the operators to take appropriate action.

4.3.1 Plants with condensate polishers (Measurement at Condensate Polisher Outlet, CPO)

Key Instrumentation:

Conductivity after cation exchange at CPO is the most important parameter because it rapidly alerts the operator to ingress of potentially corrosive anions and is more sensitive than conductivity.

A sample is taken from the polishing plant outlet (each bed in the case of parallel streams), upstream of subsequent dosing.

Additional Instrumentation:

Conductivity measurement at CPO is valuable to provide confirmation of the effective operation of the polisher and to alert the operators to the need for regeneration of the resins.

Sodium at CPO rapidly alerts the operator to cation breakthrough and hence to the need for regeneration of the resins. In this context it is more sensitive than conductivity. For plants operating with condensate polishers in the ammonium form, the addition of sodium monitoring at CPO will ensure protection from contamination of feedwater by residual regenerant. In this instance the sodium monitor becomes a Key Instrument.

4.3.2 All Plants (with or without condensate polishers) (Economizer Inlet, EI, on conventional plants, and downstream of the feed pumps on HRSG plants)

Key Instrumentation:

Conductivity measurement at EI is essential to give a rapid indication of the successful operation of dosing systems to control feedwater pH. This is conventionally measured at these locations.

Conductivity after cation exchange is also monitored at these locations in order to confirm that no contaminants have entered the feedwater with the dosed alkali (ammonia or amine), through condenser leakage or via any other route.

pH measurement (or assessment from conductivity and conductivity after cation exchange) provides further confirmatory information that the dosing regime specified for the plant is being achieved.

Dissolved oxygen is measured to confirm its satisfactory control within the target regime for the plant. In those units where oxygen dosing to the feedwater is practiced, it is essential to confirm that the target range is being achieved at the economizer inlet. Although it is common practice to use a single instrument to monitor a number of locations, a dedicated instrument will be required in circuits where the dissolved oxygen concentration is closely controlled.

ORP measurement at deaerator inlet, DI, or in the absence of a deaerator at EI is used to provide valuable information for the operators of plant that has copper alloys present in the feed circuit. (Note that this technique is only included in the Key Instrumentation set for this group of plants and not for units which have no copper alloys.)

The following **Optional Additional Instruments** may be included for feedwater monitoring:

Dissolved oxygen may be measured upstream and downstream of the deaerator to confirm its satisfactory operation. The use of a single instrument switched between two or more sample points may be appropriate and where a high degree of confidence in deaerator performance has been achieved further regular measurements may not be justified.

4.4 Drum Boiler Water/HRSG Evaporator Water

The detailed requirements for monitoring boiler drum waters vary according to the chemical regime in use.

Ideally, samples are taken from appropriately designed sampling probes in the boiler downcomers. However it is common to find samples taken from the boiler blowdown lines. This practice is really only satisfactory if flow in the blowdown line is continuous. It inhibits the option of operating the plant without blowdown when contaminant ingress rates are low.

The choice of the downcomer sample point location is particularly important for drum boilers operating with oxygenated chemistry regimes.

4.4.1 Drum boiler plants with AVT (no solid alkali being added to the drum)

This section is applicable to the drums on conventional fossil plants and on combined cycle/HRSG plants.

The use of all-volatile treatment, AVT, implies very rigid restrictions on contamination levels in the boiler.

The following instruments should be included in the **Minimum Key Level:**

Conductivity measurement is valuable to provide a warning of deviation from the normal operation of the boiler. In sliding pressure operation it must be recognized that volatile dosing agents will favor the steam more strongly as pressure falls and thus the equilibrium state of the boiler dosing will be pressure dependent.

Conductivity after cation exchange is monitored in order to confirm that no contaminants are accumulating to an excessive level in the boiler water and to guide the operators on the adjustment of blowdown rates.

pH measurement provides further confirmatory information that the dosing regime specified for the plant is being achieved.

The following **Optional Additional Instruments** may be included for drum water monitoring under AVT chemistries.

Silica may be measured in the boiler water if the relationship between its concentrations in water and steam are known. (Although the aim is to control silica levels in steam, the measurement in boiler water may be more reliable in some circumstances.) Note, however, that the relationship between silica in drum water and in steam may change according to load, pressure, drum water level, condition of drum furniture, etc. so that the of concentration in steam remains the Key Measurement.

4.4.2 Drum boiler plants with phosphate treatment

This section is applicable to the drums on conventional fossil plants and on combined cycle/HRSG plants when phosphate is the treatment of choice. Phosphate chemistry may be rather complex in a practical boiler with other contaminants present and with the risk of phosphate hideout processes occurring. A full description of the boiler chemistry cannot be attained without comprehensive analysis of the concentrations of sodium, phosphate, and all of the other ionic species that may be present at significant concentrations (chloride, sulfate, carbonate, ammonium, etc.). A pragmatic approach is normally essential.

The following instruments should be included in the **Minimum Key Level**.

Conductivity measurement again provides a warning of deviation from the normal operation of the boiler. In boilers where high levels of phosphate hideout occur, there can be large increases in conductivity during periods of low load operation.

Conductivity after cation exchange is of some value in this dosing regime despite the complicating factor that results from the contribution of the phosphate anion. When potentially corrosive contaminants such as chloride are present, the conductivity after cation exchange rises appreciably more rapidly than the conductivity. However, it is acknowledged that measurements of conductivity and conductivity after cation exchange without additional information on phosphate and contaminant ion concentrations cannot yield a full and unambiguous understanding of the behavior of the boiler water. Complete interpretation of the measurement requires, at least, knowledge of pH and is simplified by knowledge of the phosphate concentration.

The use of cation membrane electric dialysis to reduce the maintenance requirements for cation exchange resin when analyzing boiler waters can be beneficial. Such techniques may be expected to find more widespread use in the future.

pH measurement is valuable because it demonstrates that the phosphate present in the boiler water is appropriate to provide the necessary control over the risks of both acidic and alkaline corrosion. At low phosphate concentrations, the measured pH at 25 ºC can be significantly influenced by the ammonia concentration. Note, however, that at higher phosphate concentrations, small condenser leaks may have only a very minor effect on the pH of the bulk boiler water. Thus pH measurement alone is an insensitive indicator of corrosion risk in phosphate dosed boilers.

Phosphate measurement is necessary to enable unambiguous control of dosing in boilers that are subject to hide-out and to allow the interpretation of the conductivity after cation exchange in terms of other contaminants. However, given the costs and the level of operator care required for the reliable use of on-line phosphate monitors, many plants that are free of phosphate ion control problems (hide-out, etc.) may operate satisfactorily without this instrumentation.

The following **Optional Additional Instruments** may be included for drum water monitoring under phosphate dosing conditions.

In circumstances where it is necessary to achieve a fuller understanding of the boiler chemistry (specifically the [sodium]:[phosphate] molar ratio which can be strongly related to corrosion risk) it becomes essential to monitor **sodium** as well as phosphate concentrations. Complete understanding of phosphate chemistry in drum boilers requires a high level of attention to the analytical techniques by the plant chemist or an appropriate specialist.

Silica may be measured in the boiler water if the relationship between its concentrations in water and steam are known. (Although the aim is to control silica levels in steam the measurement in boiler water may be more reliable in some circumstances.)

4.4.3 Drum boiler plants with caustic treatment

This section is applicable to the drums on conventional fossil plants and on combined cycle/HRSG plants when NaOH is the alkalizing treatment of choice.

The monitoring of sodium hydroxide dosing regimes in drum boilers is generally simpler than the phosphate case, but it is essential to include measures to alert operators to any over-dosing, which can itself carry a corrosion risk for the boiler waterwalls and also for the steam turbine (by carryover).

The following instruments should be included in the **Minimum Key Level**:

Conductivity measurement generally provides a direct indication of the dosed concentration of hydroxide. Its measurement can be used as a key parameter in the adjustment of boiler blowdown rates and dosing system setting.

Conductivity after cation exchange gives a clear indication of the accumulation of impurity anions in the boiler water and therefore provides additional information on which to base control of the blowdown system.

pH measurement provides confirmatory information that the target dosing regime is being achieved.

The following **Optional Additional Instruments** may be included for drum water monitoring under sodium hydroxide dosing conditions.

Silica may be measured in the boiler water if the relationship between its concentrations in water and steam are known. (Although the aim is to control silica levels in steam, the measurement in boiler water may be more reliable in some circumstances.) Note that silica is less volatile in boilers with caustic dosing than in AVT dosed units.

4.5 Once-through boilers

Once-through boilers require treatment exclusively with volatile dosants in order to eliminate the risk of added chemicals concentrating at dry-out. Regimes may be reducing (conventional AVT, AVT(R)), oxidizing (conventional AVT, AVT(O)), or oxygenated (OT). Both conventional subcritical and supercritical plants and combined cycle/HRSG plants with once-through boilers are covered.

The main monitoring requirements for once-through boilers are covered in the feedwater section above.

The use of steam separator vessels provides an opportunity for monitoring any potential accumulation of contaminants at dry-out on the evaporator tube surfaces. Measurement of **conductivity** and **conductivity after cation exchange** of water sampled from the separator vessel drain can provide a valuable warning of ingress of contaminants to the circuit.

4.6 Steam

This section is applicable to drum boilers on conventional fossil plants and on combined cycle/HRSG plants, and to once-through units.

In drum boilers of conventional and HRSG plants the steam may be sampled at two locations:

The first is upstream of superheaters; saturated steam in this part of the plant may contain entrained water droplets and this requires specific consideration of sampling probe design.

The second is downstream of the superheaters; superheated and reheated steam is free of droplets and may contain solutes derived from attemporator sprays. The sample cooling requirements are more arduous for the superheated steam.

In once-through boilers superheated and/or reheated steam sampling are the only practicable options.

Steam is monitored to ensure adequate purity, free from excessive carryover of boiler solutes (drum boilers only), free from solutes derived from contaminated spray water and free from unacceptable concentrations of silica which could form deposits in turbines.

The following instruments should be included in the **Minimum Key Level**.

4.6.1 Main Steam – Saturated

Provided that appropriately designed sampling probes are in place, the monitoring of **sodium** concentration and **conductivity after cation exchange** provides information on the risk of carryover of solutes from the boiler into the steam turbine. Targets may be set for both parameters and operational changes may be required in order to ensure compliance. Persistent elevated values may indicate mechanical damage within the boiler drum.

In many plants, good control over the risk of carryover is consistently achieved and operators may wish to reduce the saturated steam monitoring level. Where comprehensive monitoring of superheated or reheated steam is practiced, the monitoring of saturated steam may be reduced to the level recommended in the IAPWS Guidance Document on Carryover [3]. However, the risk of deterioration of steam purity does not diminish over the lifetime of the plant. It may result from a number of causes and therefore complete suspension of all steam monitoring is not recommended.

Technically, superheated steam or reheat steam is preferred to saturated steam for continuous on-line monitoring. However, as indicated in the parallel IAPWS Guidance Document on Carryover [3], the saturated steam location may be used to record carryover on a frequent, but non-continuous basis.

4.6.2 Main Steam – Superheated and Reheated

Targets for superheated and reheated steam may be more directly related to the conditions that are acceptable within the steam turbine. Some deposition within superheaters and reheaters can result in a short-term reduction of concentration of non-volatile contaminants but, during prolonged operation at steady load, equilibrium will become established.

The sampling point may be at the superheater outlet or at the reheater outlet. The latter provides information on steam purity downstream of all locations where feedwater is added to steam (attemporators) and therefore provides data that are responsive to any contamination of the spray water. However, additional deposition of solutes that have low solubility in steam occurs at the lower pressure in reheaters and this can prejudice the results.

The monitoring of **sodium** concentration and **conductivity after cation exchange** provides information on the risk of carryover of solutes from the boiler and of contaminants from spray water into the steam turbine. Targets may be set for both parameters and operational changes may be required in order to ensure compliance.

Persistent elevated values may indicate mechanical damage within the boiler drum or feedwater contamination. Both circumstances require operator intervention to identify and mitigate the problem.

The monitoring of **silica** concentration provides assurance that the plant can be operated with adequate control of the risk of silica deposition in steam turbines. In those plants where the make-up water contains non-reactive silica, monitoring of the main steam may provide the most reliable information on the need for remedial actions.

5. Off-line batch (grab) and confirmatory analyses

It will be necessary on occasions to perform additional off-line analyses to confirm satisfactory operation of plant or to diagnose the causes of deviations from targets. It is important to note that if a plant has the Minimum Key Level of Instrumentation then there is no absolute requirement for operators to conduct a frequent grab sampling matrix of parameters to “check” on-line instruments.

Under the direction of the Plant Chemist or supervisor responsible for chemistry, grab sampling should be conducted whenever it is required for troubleshooting or when contaminant enters the cycle as indicated by the Minimum Level of Instrumentation.

Additional collection and analysis of grab samples on a periodic basis during prolonged periods of normal operation within guideline targets will reinforce plant operation by ensuring that appropriate procedures are in place and that operating/chemistry staff retain familiarity with them.

The techniques that can be deployed are many and varied. They should be matched to the specific application.

Iron. Monitoring total iron (soluble plus particulate) concentrations provides assurance that the rate of transport of corrosion products into the boilers and onto steam turbine blading is kept within acceptable limits. It also can demonstrate whether the steam/water circuit is potentially suffering from flow-accelerated corrosion, FAC. The techniques used must be capable of discrimination of iron at concentrations of 1 to 5 $\mu g \cdot kg^{-1}$ and of quantification of iron at much higher concentrations

Copper. Many older plants have copper alloys in condensers and in the feedwater heaters. Copper can readily be oxidized into a mobile form and can subsequently deposit within evaporator tubes or, in a high pressure plant, on steam turbines. Batch analysis of feedwater can be used to establish whether effective control over copper transport is being achieved.

Ionic Contaminants. When it becomes necessary to identify the source of contaminants in the steam-water circuit that are responsible for increases in conductivity (direct or after cation exchange), the use of ion chromatography can provide particularly valuable information. By appropriate choice of analysis columns and eluents, it is possible to discriminate and quantify a wide range of cations and anions (including organic acid anions).

6. References

1. IUPAC, *Quantities, Units and Symbols in Physical Chemistry*. (RSC Publishing, 2007).
2. ISO Standard 105234:2008. *Water quality – determination of pH*.
3. IAPWS Technical Guidance Document, *Procedures for the Measurement of Carryover of Boiler Water into Steam* (2008), available from www.iapws.org.

Table 1 Summary of Minimum Key Instrumentation requirements.

A range of additional optional instrumentation may be required on plants which have non-generic problems. Their use, as covered in the text above, will be plant-specific and subject to local considerations.

Sampling location		**Minimum Key Instrumentation**	**Caveat**
Condensate Pump Discharge (CPD)		Conductivity after cation exchange	
		Dissolved oxygen	
		Sodium (Key on seawater-cooled plants)	Not plants with air-cooled condensers
Feedwater (Drum and Once-through boiler circuits)	Condensate Polisher Outlet (CPO)	Conductivity after cation exchange	
		Sodium (Key Instrument if CPP is operated in ammonia form)	
	Economizer Inlet (EI) or main feed pump (HRSGs)	Conductivity	
		Conductivity after cation exchange	
		pH	
		Dissolved oxygen	
	Deaerator inlet	ORP	Plants with copper alloys in feedwater circuit.
Boiler drum Downcomer (preferable) or blowdown	Plants on AVT and those on Caustic treatment	Conductivity	
		Conductivity after cation exchange	
		pH	

Sampling location		Minimum Key Instrumentation	Caveat
	Plants on OT	Conductivity Conductivity after cation exchange pH Dissolved Oxygen	Sample should be from downcomer.
	Plants on phosphate treatment	Conductivity Conductivity after cation exchange pH Phosphate (plants that prove vulnerable to hide-out or to other issues with phosphate concentration control)	$[\mathrm{Na}]:[\mathrm{PO}_4]$ molar ratio measurement may require additional monitoring. Data interpretation based on conductivity and CACE measurements alone may be ambiguous.
Steam	Saturated	Conductivity after cation exchange Sodium	Iso-kinetic sampling is necessary.
	Superheated/ Reheated	Conductivity after cation exchange Sodium	
		Silica	For plants that have consistently demonstrated a low risk of elevated silica concentrations in steam the continuous monitoring may be considered inessential.
Make-up water plant outlet		Conductivity	
		Conductivity after cation exchange	Plants with storage tank exposed to atmosphere.
		Silica Total Organic Carbon	Plants where there is a risk of non-reactive silica or organic contamination of raw water.