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Technical Guidance Document:

Corrosion Product Sampling and Analysis for Fossil and Combined Cycle Plants

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President:
Professor Tamara Petrova
Moscow Power Engineering Institute
Moscow, Russia

Executive Secretary:
Dr. R. B. Dooley
Structural Integrity Associates
Southport, Merseyside, UK
Email: bdooley@structint.com

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This technical guidance document considers the sampling and monitoring of total iron and copper corrosion products in fossil and combined cycle/HRSG plants.

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

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1 Nomenclature and Definitions

Term	Alternative or Acronym	Definition
All-volatile Treatment	AVT AVT(R) AVT(O)	Conditioning regime in which only volatile alkalizing agents are added to the feedwater (commonly ammonia, but other volatile amines may also be employed) May be either: Reducing conditions (added reducing agent) or Oxidizing conditions (without reducing agent)
Air-cooled Condenser	ACC	System to condense steam from a turbine by indirect air cooling
Condensate		Water that derives from condensation of steam after expansion in a steam turbine and passage through a condenser or process heat exchanger. "Main condensate" refers to the condensate from the turbine condenser including its possible tributaries up to the end of LP feedwater heaters
Conductivity	Specific Conductivity Direct Conductivity	Electrical conductivity of the water sample as measured directly without any treatment [1]
Conductivity after cation exchange	CACE Cation Conductivity Acid Conductivity	Conductivity of a water sample after passage through a strongly acidic cation exchanger in the hydrogen form
Caustic Treatment	CT Hydroxide Dosing	Involves addition of NaOH to the boiler or HRSG evaporator
Drum boiler		Boiler in which steam (generated in heated evaporator tubes) is separated from water in an unheated horizontal pressure vessel (drum). The liquid phase is recirculated to the evaporator.

Term	Alternative or Acronym	Definition
Feedwater		Water that is being pumped into a boiler or HRSG to balance the steam production; usually understood as water passing from the deaerator and/or the high pressure heaters to the boiler
Flow-accelerated Corrosion	FAC	Accelerated corrosion of carbon steel components in the feedwater system and HRSG evaporators caused by chemical dissolution of magnetite on the surface and exacerbated by turbulence in the flow
Heat Recovery Steam Generator	HRSG	Plant that generates steam using heat transfer from the exhaust gas of a combustion (gas) turbine
Once-through boiler or HRSG		Boiler in which output steam is generated from input water by complete evaporation. There is no recirculation of boiler water.
Oxygenated Treatment	OT	Conditioning regime in which ammonia and oxygen are added to the feedwater
ppb, ppm	µg/kg, mg/kg	Fraction of the quantity of a substance in another substance (quantity per quantity). In power cycle chemistry commonly used for describing the mass fraction (mass per mass) of a substance in steam or water. Its use as "concentration" (quantity per volume) is ambiguous and formally incorrect.
Phosphate Treatment	PT	Conditioning regime for drum boilers in which alkalinity is achieved by dosing tri-sodium phosphate to the boiler water

2 Technical Guidance Document Key Information Summary

The key information contained in this technical guidance document is summarized in Table 1

Table 1: Summary of key information related to corrosion product sampling and analysis

Aspect of a Successful Corrosion Product Sampling Program		Description	Comment
1	Forms of corrosion products	Corrosion products take the form of particulate and dissolved for both iron- and copper-based materials	Particulate + dissolved = total corrosion products
2	Corrosion product achievable limits	Dependent on plant design, cycle chemistry and system metallurgy	Refer to Section 5
3	Rationale for corrosion product sampling	To determine the effectiveness of the cycle chemistry treatment program	Also used to determine the effectiveness of any changes to a cycle chemistry treatment program
4	Corrosion product sampling location	As per Table 2. Actual locations dependent on plant and cycle design	There is normally no requirement for the sampling of corrosion products in steam. This Technical Guidance Document is for corrosion product sampling from the water phase for conventional fossil or combined cycle plants
5	Corrosion product sampling – unit operating conditions	Plant at stable operation and similar load conditions for each sampling period. Greater than 80% to full load suggested	Sampling during transient plant operating conditions or during different plant operating conditions is ineffective for providing robust corrosion product data for analysis. Sampling at fixed times is not sufficient. Plant operating conditions dictate sampling frequency
6	Corrosion product sampling frequency	1 to 2 weeks of corrosion product sampling every 6 months	Continuous/routine sampling of corrosion products is not required. Sampling length and frequency may be increased during periods of major cycle chemistry changes
7	Sample conditioning system for corrosion product sampling	As per Table 4	Turbulent flow or the highest possible sustainable flow rate at the time of corrosion product sampling in all locations of the sample conditioning system is critical for effective sample collection
8	Corrosion product grab sampling methodology	As per Table 5	Single-use bottles suitable for low level metals analysis and preserved with nitric acid are recommended

Aspect of a Successful Corrosion Product Sampling Program		Description	Comment
9	Corrosion product integrated sampler sampling system	As per Figure 2	Sampling during transient plant operating conditions or during different plant operating conditions is ineffective for providing robust corrosion product data for analysis. Sampling at fixed times is not sufficient. Plant operating conditions should dictate sampling frequency. Turbulent flow or the highest possible sustainable flow rate is required during all sampling periods
10	Particulate corrosion product digestion and analytical methods	All particulate corrosion products in a sample require digestion to be converted into the dissolved form prior to analysis	Utilization of heat, acid and time are required to ensure complete digestion. As per Section 9.1
11	Corrosion product analytical methods	As per Table 6 for iron and Table 7 for copper	The selection of an analytical method with a suitable detection limit is critical

3 Introduction: Purpose of Document and How to Use it

IAPWS has recently issued a series of Technical Guidance Documents for the cycle chemistry control of conventional fossil and combined cycle plants.[2,3,4,5] These documents (including this one) can be applied to co-generation plants as well as those conventional and combined cycle plants. The volatile treatment and phosphate/caustic documents include suggestions for the levels of corrosion products at key locations around the plant cycle. When a particular plant has the cycle chemistry optimized, the general corrosion and flow-accelerated corrosion (FAC) in the feedwater, condensate, and low temperature circuits where attack can be the highest should be minimal. Otherwise, components such as feedwater and condensate piping, and tubing in the low pressure circuits of HRSGs, can become thin and ultimately fail. The corrosion produces iron oxides in all plants and copper oxides in plants with mixed-metallurgy materials, the latter most often including copper-based alloys in feedwater heater tubing. The corrosion products consist of both dissolved and particulate oxides, which are transported throughout the water-steam cycle and deposit on higher pressure heat transfer surfaces. These deposits can impede heat transfer, affect the performance of the boiler, HRSG or steam turbine, and most importantly they can act as initiating centers for other failure/damage mechanisms such as under-deposit corrosion (UDC) on boiler waterwalls and HRSG evaporator tubing.

It should be noted that the feedwater and boiler/evaporator treatments for the conventional and combined cycle/HRSG plants have been published in previous IAPWS Technical Guidance Documents.[4,5] The Normal/Target values promulgated in these documents and customized as needed, consistent with the plant characteristics, are expected to produce the minimum levels of corrosion products and thus these values remain the same.

This Technical Guidance Document is designed to supplement the IAPWS documents on water treatment to ensure that corrosion products are monitored using adequate and effective sampling and analytical techniques. It can be used directly by chemists and plant operators, and will be

useful for the development of guidelines at the international, national, company and manufacturer level. It can also be used in the design phases of generating facilities to ensure that the optimum sampling locations are provided and that there is appropriate analytical equipment for the chemistry laboratory and/or steam/water sampling systems (sometimes called wet racks).

The primary purposes of this document for use in fossil and combined cycle/HRSG plants are to:

a) highlight the problems that can exist with the physical sampling of corrosion products in flowing water and steam,
b) indicate how these problems occur and can be avoided,
c) indicate the key plant locations where sampling should be conducted,
d) provide an outline of an optimum sampling system for the representative sampling of corrosion products,
e) highlight the various analytical methods that can be used for the analysis of corrosion products with the advantages and disadvantages of each method clearly outlined,
f) suggest a level of quality control to ensure reliable analysis.

It is emphasized that this is an IAPWS Technical Guidance Document representing the cumulative experience of IAPWS PCC Working Group members worldwide. It provides guidance on the best practices for sampling and analyzing corrosion products to indicate that the chemistry treatments and operating regimes customized for a plant are optimal, and that general corrosion and FAC are minimized. Performing these tasks properly provides the operator/chemist some assurance that the plant is not likely to fail and is safe for the plant personnel. The guidance document can form the basis of, but should not restrict, other derivative guidelines around the world. Experience has indicated that, depending on local requirements, the processes and procedures described in Section 6 will provide good reliability and availability if they are customized for each plant depending on the actual conditions of operation, the equipment installed, the materials used in different parts of the cycle, and the condenser cooling media.

It is further emphasized that these guidance values should not be considered as manufacturer's guarantees. Adoption of the optimum sampling and analytical processes described in this TGD may provide levels of iron and copper corrosion products that are different from those suggested by manufacturers. Each manufacturer should provide a set of target values representing the plant as designed, and these may be slightly different from the operating guidance provided in this document.

Throughout this document, conductivity limits are provided in units of µS/cm and concentrations in µg/kg. It is recognized that conductivity units of µS/m are preferred in the SI unit system; this document uses µS/cm to be consistent with the most common industrial practice worldwide. All conductivities and pHs in this document refer to water samples controlled to 25 °C.

4 Background to Dissolved and Total Corrosion Products

Corrosion products can circulate in the water-steam cycle in dissolved and particulate states.

Dissolved Corrosion Products means that the corrosion product (iron, copper, etc.) is present in ionic form or as simple (e.g., monomeric, dimeric) hydrated species in the sample at the time of sample collection.

The aqueous corrosion of a metal immediately forms positive metal ions (cations) at its surface. This is an oxidation (anodic, in electrochemical terms) process involving the release of electrons that react with the oxidant close by on the surface. The oxidant will be just the water in a deaerated environment or dissolved oxygen in an aerated environment, and its reaction with electrons is the balancing reduction (cathodic, in electrochemical terms) process that typically forms negative ions (anions) such as hydroxide. The cations combine with the anions and form a corrosion product layer of oxide on the surface while some stay in solution and are transported to the bulk fluid. There, they may stay in solution or some may precipitate as particles of oxide in suspension. Also, depending on the chemical and physical condition of the fluid (pH, temperature, flow rate), the oxide film itself may tend to dissolve or release particles by erosion. The overall process is clearly dependent on the oxidation-reduction potential (ORP) of the fluid. ***Particulate Corrosion Products*** are suspended particulate solids (usually oxides or hydroxides) at the time of sample collection. They might precipitate directly in the fluid phase or be released from the layer on the metal surface in water-touched components, or during an electrolytic (galvanic) corrosion process as end products of the electrochemical reaction.

The relationship between Dissolved, Particulate and Total Corrosion Products is given in the following equation:

Total Corrosion Products = Dissolved Corrosion Products + Particulate Corrosion Products

In all cases the corrosion products originate from corrosion processes and either type can transform into the other, depending on the chemical and physical conditions at the various locations in the water-steam cycle. For example, the solubility of iron ions in flowing water in a temperature range of 50–300 ºC is strongly influenced by pH and temperature, so precipitation and dissolution can occur around a circuit.

Such transformations often take place at locations in the water-steam cycle where the conditions change continuously or drastically. This is the case for example in the turbine during steam expansion. Temperature and pressures drop steadily with the result that the steam becomes oversaturated for example in copper. Copper (oxide/hydroxide) precipitation follows on the high pressure (HP) turbine blades, which can result in reduced efficiency, increased axial thrust, increased vibrations, etc.

Similar phenomena can be observed for iron cations in the condensate level-control valves of the HP and LP pre-heaters, where the pressure is reduced drastically. As a consequence, the condensate at boiling point partly evaporates (flash-effect). This adiabatic expansion leads to a drop in temperature of the remaining condensate. Oversaturation of the condensate in iron

cations might be the result, followed by precipitation of magnetite (Fe_3O_4) in the valve body or cage that finally leads to malfunction of the valve.

Therefore it is good practice to analyze, monitor, and try to minimize the amount of dissolved and particulate corrosion products in the condensate, feedwater, and boiler/evaporator water at various locations in fossil and combined-cycle/HRSG power plants. Note that assessing particulate concentrations involves sample filtration, so the practical definition of particles in terms of their size depends on the pore size of the filter medium. Common definitions for power plant cycles are 0.45 µm and 0.20 µm. It follows that "dissolved" corrosion products involve all those that pass through the filter, even though they will contain very small particles. Section 5 provides advice on sampling locations, frequency and strategy.

5 Corrosion Product Sampling, Rationale and Sample Locations

The results from sampling and analysis of corrosion products in fossil and combined cycle/HRSG plants provide the fundamental indicator of whether there is an effective cycle chemistry program in place for any steam raising plant while it is at a referenced operating condition which is the same for each sampling period; e.g., steady operation at full load. The same processes should be used to assess any changes to the chemistry treatments or to operating guideline values in efforts to optimize the plant cycle chemistry.

To provide an indication of the levels of corrosion products in some of the main fossil and combined cycle/HRSG plants, the following points are delineated to provide some guidance in the other sections of this document. Note that the values provided are for steady state, full load, operation only and not for any transient conditions.

- Fossil plants with all-ferrous feedwater systems. Monitoring corrosion products at the economizer inlet provides an indicator of whether the feedwater treatment is appropriate and whether there is any FAC occurring. As covered in the IAPWS treatment TGDs, the level of total iron at this location is dependent on the feedwater treatment. Levels below 1 µg/kg for units on oxygenated treatment and below 2 µg/kg for units on AVT are typically easily achievable with optimized cycle chemistry.

- Fossil plants with mixed-metallurgy feedwater systems. Monitoring corrosion products at the economizer inlet provides an indicator of whether the feedwater treatment is appropriate, whether there is any FAC occurring, and whether the copper alloys in the feedwater heaters are protected. As covered in the IAPWS treatment TGDs, the levels of iron and copper at this location are dependent on the feedwater treatment. Levels of total iron and copper below 2 µg/kg for units on AVT are typically easily achievable with optimized cycle chemistry.

- Fossil plants with all-ferrous and fossil plants with mixed-metallurgy feedwater systems. As indicated in the IAPWS TGD for volatile treatments, monitoring the cascading drain lines provides an indicator of whether two-phase (steam-water) FAC is controlled. It is most effective in these situations to monitor the drain from the lowest high pressure (HP) heater. Levels of total iron (dissolved and particulate) below 10 µg/kg are typical for optimized cycle chemistry with feedwater pHs around 9.8.

- Combined cycle/HRSG plants. Monitoring corrosion products in the feedwater and evaporator drums provides an indication of whether single- and two-phase FAC are controlled in the preheater (low pressure (LP) economizer), LP evaporator, LP risers and drum components, IP and HP economizer, IP evaporator, and IP evaporator and risers. Often for HRSGs it is sensible to monitor total iron at the inlet and outlet of the preheater and LP economizer circuits. As covered in the IAPWS treatment TGDs, the level of total iron at these locations is dependent on the feedwater and condensate treatments. Levels of total iron less than 2 μg/kg in the feedwater and less than 5 μg/kg in each drum are typically easily achievable with optimized cycle chemistry.

- Fossil plants and combined cycle/HRSG plants in general. Monitoring steam for total iron levels provides no indication of the condition of the cycle chemistry control and is ineffective as a means of drum carryover detection. Monitoring steam for copper in units with mixed-metallurgy systems is dependent on the drum pressure and the solubilities of the cuprous and cupric hydroxides. As suggested in the IAPWS TGD on Steam Purity,[6] the copper level in steam is dependent directly on the feedwater chemistry, and once this is optimized and the copper levels at the economizer inlet are around 2 μg/kg then copper levels in saturated steam and main steam should consistently also be less than 2 μg/kg. Note that there are no target values in the IAPWS TGDs for either Fe or Cu in steam.

- Fossil and combined cycle /HRSG plants with air-cooled condensers (ACC). Monitoring corrosion products in the condensate before and after a condensate filter provides an indicator of whether corrosion and FAC are minimized in the ACC at the tube entries in the upper transport ducts (streets). As covered in the IAPWS volatile treatment document, the level of total iron (dissolved and particulate) at these locations is directly dependent on the feedwater/condensate pH. Levels of total iron below 10 μg/kg are consistently achievable with pH levels around 9.8. Downstream of a typical filter (5 μm absolute) the levels can be consistently controlled to around 5 μg/kg.

- Cogeneration plants with condensate return systems. For a cogeneration plant that sends steam to a steam host for use in a process (either via direct or indirect use) and then receives all or a portion of the condensate back, monitoring corrosion products in the return condensate indicates whether corrosion and FAC are minimized in the process part of the steam host plant. High corrosion product levels in return condensate in cogeneration plants are not uncommon. It is common for condensate filters to be utilized in cogeneration plants prior to the condensate being returned to the boiler or HRSG system. Levels of total iron below 10 μg/kg are consistently achievable with pH levels around 9.8 for all-ferrous plants. As indicated above, downstream of a filter (5 μm absolute) the levels can be consistently found to be around 5 μg/kg. For mixed-metallurgy plants the copper levels can be extremely variable depending on the plant design and operation, but with the chemistry optimized as far as possible levels of total copper less than 10 μg/kg can be expected.

Table 2: Summary of key corrosion product sampling locations

Type of Plant	Sampling Locations								
	ACC Outlet*	Condensate Filter Outlet*	Condensate Pump Discharge	Process Condensate Return	LP & HP Heater Drains	Dearator Inlet	Economizer Inlet	Boiler /Evaporator	Saturated or Superheated Steam
Fossil – All Ferrous	X	X	X		X		X		N/A
Fossil – Mixed Metallurgy	X	X	X		X	X	X		N/A
Combined Cycle/HRSG Plants	X	X	X				X	X	N/A
Cogeneration Plants	X	X	X	X			X	X	N/A

* If ACC or condensate filters installed

It should also be noted here that there should never be a reason to sample and analyze corrosion products on a frequent basis (daily or weekly) once the operator/chemist has used the other IAPWS TGDs to customize and optimize the chemistry in the plant. Sampling over a period of one to two weeks every six months will be adequate to check that the levels are approximately as indicated above. Only in the case of some major chemistry changes in the plant should the frequency of the sampling be increased. Corrosion product monitoring should be undertaken with the plant in the same condition for each sampling period. The plant should be at greater than 80% of full load and stable for a minimum of two hours prior to sample collection, with all sampling taking place under similar conditions. Corrosion product monitoring should be used as a key performance measure when the plant challenges the status quo of the chemistry used previously and plans to change either the treatments or the guideline values. Sampling under transient plant operating conditions is not as useful as steady-state sampling, as the variability in corrosion product levels due both to actual corrosion rates varying and to sampling system errors during transients makes a meaningful analysis and comparison of any data generated impossible.

The previous bullet points have delineated typical plant locations affected by corrosion products and the approximate levels of corrosion products found there. However, not all plants sample from these locations or can achieve the levels indicated. In assessing plants worldwide, the experience of the IAPWS PCC is that there are a number of deficiencies in sampling and analyzing corrosion products. These are listed here and are the foci of the other sections within this TGD:

- No testing of corrosion products to validate a chemistry treatment. Such testing is especially important for proprietary treatment chemicals, where the plant does not know their compositions.

- Inadequate locations for sampling. The minimum requirements (outlined in the bullet points above) to determine whether the cycle chemistry is optimum are then not met.
- Improper design of sampling system and improper sampling procedures.
- Levels of corrosion products monitored and recorded much higher than the typical levels provided above and in other IAPWS TGDs, and higher than those specified in the local guidance that might be from the manufacturer or from the regional authority.
- Corrosion products sampled at the same time of day or shift, irrespective of the operating condition of the plant. One day the plant at that time could be in startup mode, at steady full load (the preferable condition for sampling), at continually changing load or in a cycling mode. Each of these regimes would be expected to provide different levels of corrosion products and thus not allow the plant personnel to compare the unit with other similar units around the world.
- Samples are analyzed using an incorrect or inaccurate technique. The most frequent deficiency here is to use a spectrophotometer with no chemical dissolution of the samples, prior to analysis, by acid digestion or heating. As indicated in Section 7, the sensitivity of the analytical techniques is often not matched to the level of corrosion products required. For example, it is not possible to use a technique that has a lower measurement limit of 9 μg/kg to determine if the chemistry is optimized for a total iron level of less than 2 μg/kg.
- No monitoring for total iron and/or copper.

6 Sampling and Sample Conditioning Systems

The purpose of this section is to provide background information for, and an outline of, an optimum sampling and sample conditioning system that provides a minimum of bias for corrosion product monitoring in fossil and combined cycle/HRSG plants. The following points (or sub-sections) have been recognized by the IAPWS PCC Working Group as providing the necessary guidance.

Only in exceptional cases will there be a sampling system dedicated to “Corrosion product sampling” alone (e.g., for a single manual grab sample line). Normally the same sample extraction, transport and conditioning equipment that is used for regular online analyses (i.e., conductivity, pH, oxygen, sodium, silica) is also used for corrosion product sampling. As a result, certain design and operating compromises are required due to economic and technical constraints linked to this dual use.

Obviously, because every plant and unit is different, customization must take place, but recognizing the custom features should eliminate some of the common major mistakes.

The sampling of high temperature fluid systems for corrosion products is complicated by the fact that both dissolved and suspended particulate corrosion products co-exist. The most common

corrosion products in fossil and combined cycle power plants are based on the oxides of iron, usually magnetite (Fe_3O_4) but mixed with hematite (Fe_2O_3) if conditions are oxidizing. Plants with mixed-metallurgy (containing both copper and ferrous materials) feedwater systems may be dominated by copper oxides in water-touched circuits. Particles range in size from a fraction of a micrometer to about 10 µm, with an average size of about 1 µm.

6.1 Sample Conditioning Systems and Limitations for Optimal Corrosion Product Sampling

Common industry standard sample conditioning systems are normally of a cost and construction optimized design consisting of the following:

1. A sample nozzle in the process stream to be sampled, isokinetic for steam samples, non-isokinetic for water-only samples
2. Single or double isolation valving for maintenance
3. Stainless steel tubing, welded or swaged, running from the sample nozzle to the centralized sample conditioning and analysis station (wet rack). This line is often field-run during construction of the overall plant and contains many bends and both vertical and horizontal sections that can result in flow restrictions and deposition of particulate corrosion products.
4. Flow rates sufficient for the online analyzers but below those required to ensure turbulent flows in all components of the sample conditioning system
5. A sample cooler at the centralized sample conditioning station followed by:
    a. Pressure reduction device
    b. Sample over-temperature protection device
    c. Sample bypass and back pressure regulating devices
    d. Sample flow indication devices
    e. Sample flow splitting devices
    f. Grab sampling device
    g. Online chemical analyzers

The operation of sampling systems such as described above for the sampling of corrosion products, without considering the requirements of effective corrosion product sampling as described in the following sections, can lead to suboptimal results. However, with due consideration of the information contained within this technical guidance document and possibly only minor modifications to existing sampling systems and their operation, more robust corrosion product sampling results can be obtained.

6.2 Design of Optimum Sample Conditioning System to Optimize Corrosion Product Sampling

The temperature gradients around the power plant circuit create differences in the solution behavior of the corrosion products – in the liquid water sections, corrosion product solubilities and dissolution/precipitation rates change from place to place. These parameters are also influenced by the chemistry of the steam-water cycle – specifically pH, which determines the electrostatic charges on surfaces and affects particle deposition as well as dissolution and precipitation from solution. The balance between particles and ions is further affected by fluid flow, since low velocities promote settling of larger particles, for example, and the behavior of particles close to surfaces is influenced by the properties of the boundary layer.[7]

The optimum place to sample for corrosion products is from a stream that has moderate to high velocity and that is downstream of, and as close as possible to, the component in the circuit that is under surveillance. These locations have been defined in Section 3. The sample point in the circuit should be at least 40 pipe diameters of straight pipe downstream from the nearest flow disturbance such as a bend, valve, orifice, etc., in order to ensure fully-developed flow. For water samples from a horizontal pipe, the sample probe should be located in the side of the pipe in an approximately horizontal arrangement.[8] Within the sampling system itself, turbulence should be guaranteed throughout – in both the hot and the cold lengths, respectively, before and after the conditioner during the periods when corrosion product sampling is being undertaken. The turbulence is estimated via the dimensionless Reynolds number (*Re*), which is the ratio of momentum forces to viscous forces in a flowing fluid. It is defined as shown in Eq. (1):

$$Re = lu\rho/\mu \qquad (1)$$

Here l is a characteristic dimension and u is a characteristic velocity for the particular situation, ρ the density of the fluid and μ the viscosity of the fluid. For a circular section pipe (e.g., main circuit piping, sample system tubing, etc.), the characteristic length used is the diameter d, and u is the bulk mean velocity. For a section with area A and mass flow rate m, $u = m/\rho A$.

Hence for a circular pipe, even if the velocity is not symmetrical with the pipe center line,

$$Re = du\rho/\mu = 4m/\pi d\mu\,. \qquad (2)$$

The second statement of Reynolds number in Eq. (2) is very useful since for many situations with steady flow along a pipe or duct with varying temperature, pressure, and cross-section the Reynolds number can be evaluated without the necessity of evaluating local velocity from the mass flow rate. For instance, for water flowing in a circular pipe with a steady mass flow rate, a reference datum may be taken as temperature 25 °C, pressure 0.1 MPa, Reynolds number of 2300 and pipe diameter d_0. For this temperature and pressure, $\mu = \mu_0$. At other locations with different temperatures, pressures, and diameters, $Re = 2300\ (\mu_0/\mu)\ (d_0/d)$.

The datum and equation given above has been used to obtain Figure 1, which shows the change of Reynolds number with temperature and pressure for a constant mass flow rate. Property

values used are from IAPWS equations, IAPWS-95[9] to provide densities at given temperatures and pressures for input to the IAPWS formulation of 2008 for viscosity.[10] The diameter of the pipe will be increased by increases of temperature and the internal-external pressure difference. These effects can be considered as small and the ratio (d_0/d) taken as unity for the figure. For water, viscosity and thus Reynolds number are strongly dependent on temperature. At low temperatures density and viscosity are for practical purposes independent of pressure. However at higher temperatures there is a significant effect of pressure.

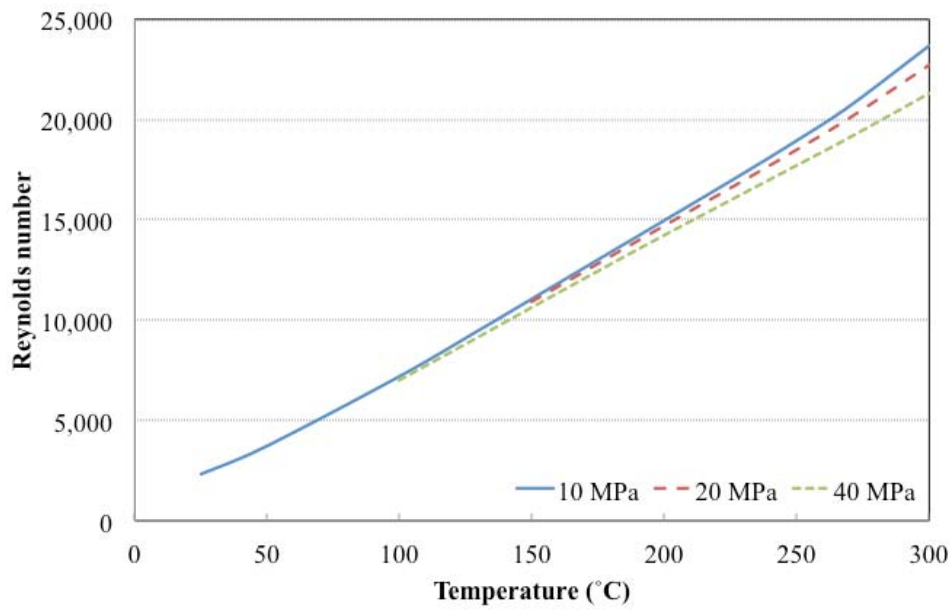

Figure 1: Relationship between Reynolds number and fluid temperature for constant mass flow in a straight tube and pressures of 10, 20 and 40 MPa. Based on densities and viscosities from IAPWS Releases.[9,10]

The 10 MPa isobar is shown for the full temperature range. If a 0.1 MPa isobar was plotted on the same graph, it would be indistinguishable from the 10 MPa isobar up to its saturation boundary of 99.61 °C. Parts of isobars for pressures of 20 and 40 MPa are given where there is significant difference from the 10 MPa line.

The Reynolds number increases by about 0.3 % with the pressure increasing from 0.1 to 40 MPa at 25 °C. At 300 °C the viscosity and the Reynolds number decrease by about 10% as the pressure changes from 10 to 40 MPa. The change in Reynolds number from the datum value to that at the highest temperature and pressure difference, due to diameter increase, is about 0.5% and is considered negligible.

In a long straight section of pipe, a Reynolds number greater than 2300 should ensure turbulent flow conditions. Figure 1 indicates how the Reynolds number at a constant mass flow changes with temperature and pressure in a straight pipe. It shows that if the sample is extracted at 25 ºC and 0.1 MPa with a Reynolds number of 2300 (i.e., just turbulent), the rest of the sample line would also be turbulent whatever the temperature and pressure, provided the criterion of Eq. (3) is met in the coil. Note that since the Reynolds number for a given mass flow is at its lowest at

low temperature, i.e., at the sample line and cooling coil outlet, so the Reynolds number must be determined there.

Higher Reynolds numbers are required to ensure turbulence in curved sections of pipe and therefore in sample lines (which have coiled sections in the coolers).[11] A correlation for the critical Reynolds number in a helical coil of tubing diameter *d* and coil diameter *D* is presented in Eq. (3):[12]

$$Re_{\text{crit}} = 2300[1+8.6(d/D)^{0.45}] \quad . \qquad (3)$$

A flow velocity greater than 1.9 m/s^{-1} at 25 ºC is normally required at the outlet for turbulent flow in standard sample conditioning systems consisting of 4 mm internal diameter sample lines and sample coolers with 50 mm coil diameters when sampling for corrosion products. Further details on the impact of sample cooler internal diameters is contained in Section 6.4.3.

Sampling systems are normally constructed with Swagelok™-type components for ease of construction and disassembly – low pressure systems would typically employ 10-15 mm internal diameter tubing and high-pressure systems 4-6 mm internal diameter tubing. The sample line isolation valves must be fully open when the sampling system is in service to minimize trapping of particulates in the valve body.

6.3 Sample Extraction for Corrosion Product Sampling

The locations where corrosion products should be sampled are included in Section 5. Here the key locations are in the water-touched circuits. During normal plant operation, the steam circuits (saturated steam and main/reheat steam) do not need to be sampled for corrosion products except in a few isolated cases usually involving copper oxides and hydroxides. If, for whatever reason, these streams are sampled for corrosion products, then the sample extraction probe needs to be isokinetic, whereas for sampling the many water streams in a power plant the sample extraction probe does not.[13]

6.4 Sample Lines – Length, Routing, Size and Flow Rate

This subsection discusses the optimum sample line configuration and suggests appropriate sampling conditions. It recognizes that many operating plants will not meet the configuration criteria, so aspects of customization may have to be considered. Many of the recommendations are contained in the ASTM Standard Practice for sampling from water systems.[14]

In sample systems for corrosion products in water-touched systems, interactions between the sample and the walls of the system inevitably lead to anomalies. A corrosion-resistant alloy such as an austenitic stainless steel (e.g., SS316L or SS316Ti) is the material of choice for constructing sample systems. Materials such as titanium or Hastelloy that contain minimal amounts of iron are occasionally used for experimental systems but are too expensive for industrial plants. Carbon steel and copper alloys should not be used for sample lines under any circumstances.

6.4.1 Sample Line Length

The sample line should be kept as short as possible. There are practical limitations to this, as the sample lines are primarily used for online water-steam monitoring which requires the samples to be directed to local subsystems where cooling water for sample conditioning is available and where a reasonable working environment for the online analyzers can be provided. The most reliable sampling of corrosion products is achieved by conditioning (cooling) the sample locally close to the sample extraction probe, with the cold line then split to a particulate sampling branch and a longer branch to the central analytical rack.

6.4.2 Sample Line Routing

Sample lines should be routed, if possible, with a continuous slope from the extraction point to the sampling station with a minimum number of bends, although the conditioner/cooler will inevitably involve a heat exchange coil. In particular, configurations such as sharp upward-downward bends or the converse, which can lead to voiding or pooling if flow transients occur, should be avoided. Bends should be gentle, with a minimum bend radius of 60 mm and, wherever possible, should be in the horizontal plane. These considerations should be borne in mind also when designing to accommodate thermal expansion of the sample line. They will minimize the general deposition of particles along the line as well as local sedimentation.

6.4.3 Sample Line Size, Curvature and Flow Rate

The sample line and entire sampling system should be sized to allow for turbulent flow and for constant flow velocities through all system components when sampling for corrosion products. The importance of maintaining turbulence and the method of assuring it via the Reynolds number of the flow in the sample line was discussed in Section 6.2 above. Thus, in a straight tube the Reynolds number must be greater than 2300 to secure turbulent flow, otherwise the flow will be laminar. The Reynolds number, *Re*, for a straight sample line is given by Eq. (2) and for a helical coil the critical *Re* depends on the dimensions as given in Eq. (3).

Typical sample coolers are made from a tube of inner diameter d = 4 mm forming a helical coil of diameter D = 50-80 mm. Using 50 mm as the worst-case diameter of the coil, the critical Reynolds number calculated via Eq. (3) is approximately 9000. This results in the need for the linear flow velocity at 25 ºC (the temperature attained at the sample cooler exit) to be greater than 1.9 m/s in 4 mm-diameter tubing and thus the volumetric flow to be greater than 87 L/hr. During normal operation the sample provided to the online chemical analyzers does not require turbulent conditions, so lower flow velocities, sufficient for the individual analyzers, can be used.

Examples of the impact of sample line internal diameter and coil diameter on the critical Reynolds number and corresponding linear flow velocity and volumetric flow are shown in Table 3.

Table 3: Calculated Reynolds numbers, linear flow velocities and volumetric flow for different sample tube inner diameters and sample cooler coil internal diameters.

		Critical Reynolds Number						
Diameter of Coil	**mm**	**40**	**50**	**60**	**80**	**100**	**120**	**150**
Tube Inner Diameter	4	9318	8648	8148	7438	6947	6581	6172
	6	10723	9918	9318	8466	7877	7438	6947
	8	11887	10971	10288	9318	8648	8148	7589
	10	12900	11887	11132	10060	9318	8765	8148
	15	15022	13806	12900	11613	10723	10060	9318

		Corresponding Linear Flow Velocity (m/s) at 25 °C						
Diameter of Coil	**mm**	**40**	**50**	**60**	**80**	**100**	**120**	**150**
Tube Inner Diameter	4	2.1	1.9	1.8	1.7	1.6	1.5	1.4
	6	1.6	1.5	1.4	1.3	1.2	1.1	1.0
	8	1.3	1.2	1.1	1.0	1.0	0.91	0.85
	10	1.2	1.1	1.0	0.90	0.83	0.78	0.73
	15	0.9	0.8	0.8	0.69	0.64	0.60	0.56

		Corresponding Volumetric Flow (L/h) at 25 °C						
Diameter of Coil	**mm**	**40**	**50**	**60**	**80**	**100**	**120**	**150**
Tube Inner Diameter	4	94	87	82	75	70	67	62
	6	163	150	141	128	119	113	105
	8	240	222	208	188	175	165	153
	10	326	300	281	254	235	221	206
	15	569	523	489	440	406	381	353

Note: Light gray numbers in Table 3 represent impractical real-world conditions (too high a volumetric flow requirement for a given Reynolds number and linear flow velocity) and should therefore be avoided due to the excessive large cooling capacity required.

In practical terms, for sampling systems that are already constructed and in service, the highest linear flow velocity that can be sustained for at least two hours prior to the collection of a corrosion product sample should be imposed. This maximum flow rate is often limited by the capacity of the sample cooler and the maximum allowable sample temperature prior to the online analyzers and will need to be determined by trial and error for each sampling system. The volumetric flow in a sampling system of known tube internal diameter and sample cooler coil diameter can be easily measured with a stopwatch and container of known volume. This result can then be used to estimate the linear flow velocity and Reynolds number from Table 3 so that an assessment of turbulence can be made.

Increased capacity sample coolers may need to be installed in some systems to enable high flow velocities. Note also that when the flow in a sampling system is changed from non turbulent to turbulent, previously settled corrosion products in the lines will be released to suspension in the

fluid. To avoid collecting the non–representative, re-entrained corrosion product bursts, sampling for corrosion products should only be undertaken after the sample lines have been continuously run at linear flow velocities of greater than 1.9 m/s (or at the maximum possible flow rate that the system will allow) for a minimum time of 2 hours.

As already mentioned, typical sampling systems for water have a tube inner diameter of 4 mm. Smaller diameters increase the risk of blocking and are difficult to install correctly. A maximum diameter of 6 mm is suggested, since larger diameters lead to lower linear flow velocities and reduced turbulence. Low pressure (LP) systems, however, need larger diameters; e.g. LP evaporator samples can only be taken if there is low pressure loss along the line, so an inner diameter between 10 mm and 15 mm is suggested. Valves and other pressure-let-down devices should be placed downstream of the sample cooler to minimize changes in the sample condition before cooling – in particular, phase distribution (e.g., water samples' flashing to steam).

Depending on the pH of the sample stream, the internal oxide and deposits on the tubing will develop a surface charge that may be similar to or different from the charge on suspended particles. Corrosion product particles may then be repelled by or attracted to the wall, so that deposition within the sample line is affected by the system chemistry. Turbulence within the fluid will tend to erode the outermost particles in a deposit as well as promote particle deposition by facilitating transport to surfaces, possibly resulting in a deposit with a steady-state thickness.

The sampling system in a new plant should be designed with effective corrosion product sampling in mind. Turbulent conditions, as determined by Reynolds number calculations, should apply throughout so that there is no drastic change in deposition characteristics along the length, particularly in the hottest sections, although it is recognized that the sample conditioner/cooler inevitably imposes some change. Transients in the sampling condition, such as a chemistry change or a surge in sample velocity, disturb the deposit and provoke a burst in measured particle concentration. Running sample lines continuously at one turbulent velocity is optimal in order to overcome such effects during system valve-in, but in any case there should be a settling-down period after any transient before a sample is taken for measurement. However, note that the higher flow rates required to ensure turbulent flows will result in large volumes of sample being run to drain, which may prove to be impractical for the plant. In that case, turbulent flow rates would only be established prior to corrosion product sampling and lower flow rates used at all other times.

Regardless of sample flow rate, sampling lines should not be isolated until the time to sample comes around, say once per shift, day, week or month, and they should be left operating with continuous flow. For both optimized and non-optimized sampling systems, in all cases it is advisable to have the sample flow running at steady turbulent conditions for at least 2 hours before a sample for analysis is collected. Another very important point is that samples should not be taken at arbitrary times, and it is strongly suggested that sampling only be conducted at times when the plant/unit has been at full load or some constant load has been maintained for 2-3 hours. Here it should be noted that sampling for corrosion products during transient conditions has very little benefit in assessing the unit condition due to complications of the effects of the transient on the sample system itself.

Oxygen in the sample stream has a strong influence on the system; as a transient constituent in fluid in contact with an alloy conditioned under reducing conditions it can be absorbed by the deposits and oxide films and may eventually oxidize them to higher species such as those based on ferric ions; these will interact differently with subsequent sample streams. The reduction to the original state after the transient is over will be a much longer process.

6.5 Sample Conditioning Systems - Cooling and Pressure Reduction

This section includes details on the optimum sample conditioning systems. The differences between conditioning the sample immediately after sample extraction and conditioning only at the water-steam sampling panel are important aspects for corrosion product sampling.

Such factors affecting corrosion products in a high temperature water-touched circuit (locations are provided in Section 5) also apply to the sample system itself. Non-isothermal conditions will certainly exist because a sample conditioning system is necessary and in fact will impose a steep temperature gradient on the sample stream in the cooler.

An optimal sample conditioning system should have the sample cooler located as close as possible to the sample extraction point with valves and other pressure let-down and temperature protection devices placed downstream of the cooler to minimize changes in the sample condition before cooling – in particular phase distribution (e.g., water samples' flashing to steam). The sample line length should be kept as short as possible. The flow split for the collection of a sample for corrosion product testing should be located after a sample over-temperature protection device. This allows for continuous flushing of this sample point without compromising overall sampling system safety.

The precipitation of dissolved corrosion products within the sample system, in particular in the sample cooler coils in the conditioning system, also leads to sampling errors. The solubility of corrosion products depends on the pH of the fluid as well as the temperature. For example, cooling a water sample at $pH_{25\,°C}$=10 (with a strong base) from 300 ºC to room temperature reduces the solubility of magnetite continuously by an order of magnitude from about 1 µg/kg, so that precipitation within the cooler is expected. Neutral water, on the other hand, sustains magnetite solubilities up to a hundred times those of high pH water, but cooling from 300 ºC to room temperature actually increases solubility by more than an order of magnitude, with a peak occurring at about 140 ºC. Dissolution of deposited particles and stainless steel corrosion products should then occur in the first section of the conditioning system, but precipitation on further cooling below 140 ºC should only occur if solubility levels are attained.[15] Clearly, the precipitation/dissolution processes when sampling neutral water systems are complex. The critical point to note here is the importance of maintaining turbulent flow under steady flow conditions, at stable plant operation prior to sampling for corrosion products. Failure to do this will compromise the reliability of the sampling results.

For maintaining turbulent flow in a sample cooler, the pressure drop at the inlet side and turbulent flow at the outlet side of the cooler need to be considered. Thus, for the cooler the largest possible inner diameter to lower the pressure drop must be compromised with the

smallest possible inner diameter to ensure the turbulence at the outlet of the cooler. This compromise is not always possible to achieve. The problem appears in the most common type of cooler – that employing a helical coil – where the coil has a strong tendency to suppress turbulence[16] (see Section 6.4.3).

Because of this tendency, much higher velocities are needed to conserve the turbulence than in a straight line, and this increases the pressure drop. For sampling from low-pressure sections of a power plant, the initial length of the coil where cooling begins and, in the case of steam lines, condensation occurs, may have to be made of larger diameter tubing to reduce pressure drop. Reverting to smaller diameter tubing for the downstream section then ensures that the cool exiting stream is turbulent. Since a larger coil diameter promotes turbulence, in double-coil coolers the outer coil should be the outlet section – again, to ensure turbulence in the cool exiting stream. Pressure reduction devices in sampling systems should be resistant to blockage and erosion damage. Needle valves in particular are susceptible to erosion if used for reducing high pressures (greater than 30 bars). Satisfactory performance can be obtained from variable-pressure reducing-element type valves. No sample line filters or strainers should be present upstream of the corrosion product sample's final collection point (end of sample line). If any type of sample filter or strainer is present in the line, it should be removed or fully bypassed prior to corrosion product sampling.

6.6 Summary of Optimal Aspects of Sample Conditioning

Table 4: Summary of optimal sample conditioning system aspects for corrosion product sampling

System Aspect		Description	Comment
1	Sample Nozzle	Non-isokinetic sample nozzle required for sampling water	Optimal location is in a straight section of pipe, 40 pipe diameters downstream of any flow disturbances
2	Sample line	Type 316L stainless steel tubing, Reynolds number for straight runs > 2300 to ensure turbulence and to avoid particle deposition	Sample line run needs to be continuously sloped and as short as practical. Line sizing needs to take pressure drop into account while ensuring turbulent flow
3	Sample line bends	Sample line bends to be gentle with a minimum bending radius of 60 mm to ensure turbulence and to avoid particle deposition	Expansion loops should be in the horizontal plane and as few as possible
4	Sample isolation valves	Should be constructed of 316L stainless steel	Isolation valves should be fully open when system is in service

System Aspect		Description	Comment
5	Sample cooler	Correctly-sized for heat transfer with the largest coil diameter possible. Critical Reynolds number for bends to ensure turbulent flow and to avoid particle deposition needs to be determined for each design	It is important to ensure turbulent flow in sample cooler. The relationship between tubing diameter and coil diameter and its impact on Reynolds number must be understood
6	Sample line liquid velocity	> 1.9 m/s for typical systems with 4 mm internal-diameter lines and 50 mm-diameter cooling coil when sampling for corrosion products. To be sustained for at least 2 hours prior to sample collection	During periods when no corrosion product sampling is occurring, lower sample line velocities are acceptable.
7	Sample line filters	Any sample line filters should be removed or bypassed prior to sampling for corrosion products	
8	Sample pressure reduction valves	Valves need to be resistant to blockage and erosion	Needle valves unsuitable for high pressure applications (> 30 bars)

7 Methodology for Optimal "Grab" Sampling of Iron and Copper Corrosion Products

Before iron and copper corrosion products can be analyzed to indicate concentrations in the process fluid, the fluid must be sampled. Incorrect sample collection can introduce significant errors into the final results.

The optimal collection methodology for a "grab" sample involves the use of a suitable sample bottle cleaned and preserved with nitric acid. High density polyethylene (HDPE) of very low metal content is recommended for the bottle and a new bottle for each sample avoids the risk of contamination. The sample line flow needs to be turbulent to ensure corrosion product particles are in suspension and should be maintained for two hours prior to sample collection (preferably continuously).

Of critical importance is that periodic corrosion product sampling should be undertaken at the same operating condition of the plant and not at the same time of day on each occasion. This ensures repeatability of the data and allows valid comparisons over time, from unit to unit, and from plant to plant worldwide.

An optimal methodology is outlined in Table 5.

Table 5: Optimal Grab Sample Methodology for Corrosion Products

Number	Optimal Grab Sampling Action	Comment
1	Obtain high density polyethylene (HDPE) bottles	HDPE is preferred but other materials may be used if suitable for use with ultra-low concentrations of metals. Bottles for corrosion product sampling are best used only once and then discarded unless they can be thoroughly cleaned and returned to an uncontaminated state
2	Clean bottles and caps thoroughly prior to use with ultrapure water	Water should be high purity with ultra-low concentrations of metals
3	Add high purity concentrated nitric acid to bottles – 0.5 mL of concentrated nitric acid for each 100 mL of bottle volume	Nitric acid minimizes the deposition of corrosion products onto the internal surfaces of the bottle
4	If sampling for total corrosion products, ensure no filters or strainers are present in the sample line	If particulate levels of corrosion products are to be determined, appropriate filtration should be done separately (see Section 8 below)
5	Open sample line valve and establish sufficient sample flow to ensure stable turbulence	Continuous sample flow is preferred. Note that once stable turbulence is established bursts of corrosion products from deposits laid down during previous periods of unstable flow will appear intermittently for an hour or so
6	Continue stable flow for two hours before sample collection	This is to establish a steady-state condition of the whole sample system.
7	Begin sampling once the unit is at the pre-defined operating condition	The plant should be at > 80% of full load for a minimum of two hours prior to sample collection.
8	Without flushing, fill the sample bottle completely and seal with lid	Flushing with the sample fluid will result in the loss of the nitric acid preservative.
9	Send sample bottle to laboratory for digestion and analysis	Samples should be analyzed without delay to minimize the risk of corrosion products attaching to sample bottle internal surfaces
10	After sample analysis, sample bottles should be discarded if they cannot be thoroughly cleaned	Sample bottles should not be re-used for future corrosion-product sampling unless they can be returned to their pristine state

8 Integrating Sampler for Iron and Copper Corrosion Products

Another key methodology for corrosion product sampling involves an integrating corrosion product sampler. This apparatus is used to obtain time-integrated, representative samples of particulate and dissolved corrosion products, with the particles being collected on an acid-digestible filter of pore size 0.1 to 0.45 µm and the dissolved fraction on an ion-exchange membrane filter placed after the particle filter. The volume of filtered sample fluid is also recorded. The sampler operates at less than or equal to 50 °C and either at system pressure or after pressure reduction. A typical version comprises a standard, high pressure filter housing

made of stainless steel and modified to accommodate two 47-mm diameter filters for particulate and dissolved corrosion products placed one on top of the other (respectively, the particle filter upstream of the ion-exchange membrane). Over extended periods the sampler collects measured quantities of particulate and dissolved corrosion products from known volumes of process fluid.

A schematic diagram of a corrosion product sampler is shown in Figure 2. An important feature of the sampler is the flow totalizer, which accurately determines the total volume of sample fluid that has passed through the filter housing, regardless of changes in sample flow rate or pressure. Control valves, pressure-reducing valves and metering devices are downstream of the filter housing to eliminate the possibility of their contributing corrosion products to the sample stream.

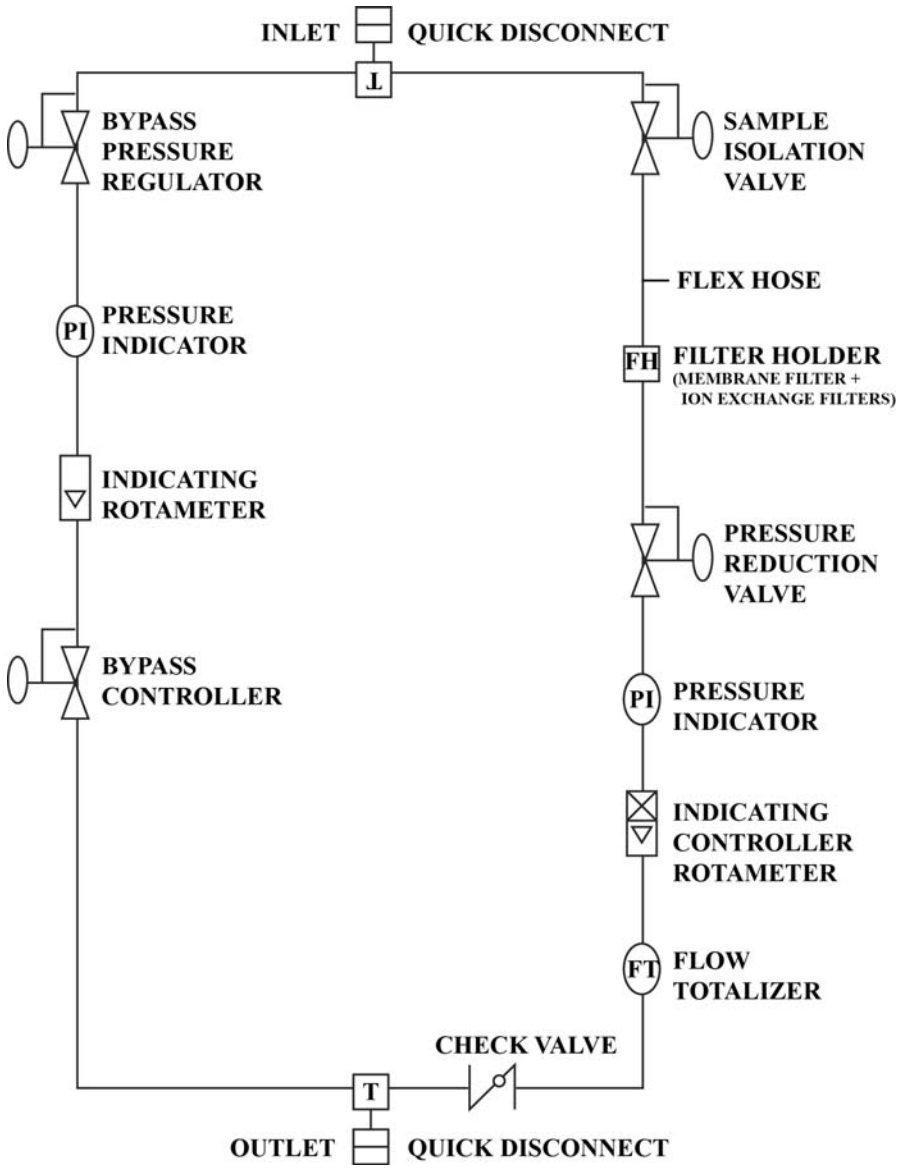

Figure 2: Schematic diagram of integrating corrosion product sampler[17]

The most effective corrosion product sampler is located as close as possible to the sample extraction point and operates with steady turbulent flow throughout the sample line for the entire

sampling duration. The sample collection period can be from 1 to 24 hours, during which the unit should maintain the same operating condition (or as close as possible to the same operating condition – for example, steady load).

After the sampling period, the filter with the collected corrosion product particles and the ion-exchange membrane filter with the collected dissolved corrosion products are removed, dried, and then digested, together or separately, in a known volume of hot acid so that all the corrosion products are dissolved. The mass of corrosion product in the acid solution is then determined via an appropriate analytical method and the result calculated back to give the concentration in the process stream. As an alternative to the ion-exchange membrane for the dissolved corrosion products, a sample may be collected downstream of the filter housing and analyzed to give the dissolved corrosion product concentration. As defined earlier, the total concentration of corrosion products is the sum of the particulate and the dissolved concentrations.

9 Analytical Methods for Corrosion Product Analysis – Iron and Copper

The possible analytical methods for iron and copper corrosion products are outlined in Tables 6 and 7. It is important to note from these tables that the best reported detection limit determines the suitability or otherwise of the analytical method for the application in question.

There are no readily available analyzers for measuring total iron and copper online continuously. Online analyzers for monitoring particles in a sample are available, but they can only reliably monitor trends (not absolute values) and cannot detect dissolved species. They include particle counters and monitors as well as turbidity meters. Since these analyzers detect and monitor the trend of particulate corrosion products in suspension, they require turbulent sample line conditions at all times.

9.1 Analytical Methods - Particulate Digestion

Analytical methods for iron or copper corrosion products are described in Tables 6 and 7. The common analytical methods require the iron to be in the ferrous or Fe(II) state and the copper in the cupric or Cu(II) state. This requirement necessitates the samples to be acidified and any particles and sampler filters or membranes to be fully dissolved prior to analysis.

A number of different digestion methods are available, with the most common being boiling nitric acid digestion[18] and 2-sulfanylacetic acid (commonly known as thioglycolic acid) digestion at 90 °C. Thioglycolic acid digestion is recommended for use with the disodium-4-[3-pyridin-2-yl-6-(4-sulfonatophenyl)-1,2,4-triazin-5-yl]benzenesulfonate analysis method (commonly known as the Ferrozine analysis method) for iron. Regardless of the digestion method, it is critical that after digestion there are no particles remaining in the sample and that all the iron and copper are fully dissolved. The digestion process can lead to loss of liquid, in which case only high purity demineralized water should be used for volume replacement.

For grab samples for total corrosion products, the sample should not be filtered either before or after the digestion step, since this will remove particulate species and result in a non-representative, low result. As indicated above, filters and membranes from integrating samplers must be fully digested as well.

Table 6: Summary of Analytical Methods for Iron

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Babcock & Wilcox Membrane Filter Comparison Charts[19]	Collection of liquid-only sample then filtering a known volume through a 0.45 µm filter under vacuum[19]	Particulate iron only. Five filter charts available for: 1. Magnetite Fe_3O_4 only 2. Hematite $Fe_2O_3.xH_2O$ 3. 2:1 Hematite: Magnetite ratio 4. 1:1 Hematite: Magnetite ratio 5: 1.5:1 Hematite: Magnetite ratio	1-L sample, cooled after pressure reduction but before sample line filters	Method is a visual comparison to a commercially available reference chart developed originally for the commissioning of once-through boilers. Separate charts available for reducing and oxidizing environments and various ratios of hematite and magnetite Approximate detection limit is 10 µg/kg Comparison-chart increments are between 15 to 250 µg/kg. **Thus technique only provides a very gross overview.**	Method is only suitable for the indication of particulate iron, primarily during new power plant commissioning. Should not be used for ongoing corrosion product analysis. **Method not accurate enough to be used in optimizing cycle chemistry on a plant.** Charts available for magnetite and hematite particulate iron oxides only.

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Ultra-Violet/Visible (UV-Vis) Spectroscopy	Colorimetric method based on Ferrozine reaction[20] – dissolved iron only	Dissolved iron, Fe, only as ions	100 mL (minimum size) sample bottle preserved with high purity nitric acid	9 µg/kg – using a standard 1 cm cell[21] 2 µg/kg – using a standard 5 cm cell[22]	Method unsuitable for determining the concentration of total iron corrosion products in untreated samples since it is for dissolved iron only. **Method not accurate enough to be used in optimizing cycle chemistry in a plant.**
UV-Vis Spectroscopy after sample digestion	Colorimetric method based on Ferrozine reaction[20] after suitable digestion step where any particulate iron oxides are converted to Fe ions	Iron ions after particulate oxides are dissolved via a digestion step	100 mL (minimum size) sample bottle preserved with high purity nitric acid	9 µg/kg – using a standard 1 cm cell[21] 2 µg/kg – using a standard 5 cm cell[22]	Minimum acceptable cell length is 5 cm. Any method utilizing a 1 cm cell is ineffective due to the 9 µg/kg detection limit of 1 cm cells. Note that most commercially available portable UV-Vis spectrophotometers are supplied with 1 cm cells only. The optimum particulate iron digestion method is to add the acid to the sample and then heat it. Examples include thioglycolic acid ($CH_2(SH)COOH$) at 90 °C or boiling nitric acid (HNO_3). Thioglycolic acid is the optimal digestion method to be used with the Ferrozine method.

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Atomic Absorption (AA) Spectroscopy after sample digestion	Flame-atomizer absorption spectrometry method after suitable digestion step where any particulate iron oxides are converted to Fe ions	Dissolved Fe after digestion step	100 mL (minimum size) sample bottle preserved with high purity nitric acid	7 µg/kg[23]	High detection limit of 7 µg/kg makes this method unsuitable for determining the concentration of iron corrosion products in power plants The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO_3)
Graphite Furnace Atomic Absorption (GF-AA) Spectroscopy after sample digestion	Graphite tube atomizer absorption spectrometry after suitable digestion step, where any particulate iron oxides are converted to Fe ions	Dissolved Fe after digestion	100 mL (minimum size) sample bottle preserved with high purity nitric acid	0.3 µg/kg[24]	Suitable for total iron corrosion products since detection limit less than optimum feedwater total iron value The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO_3)
Inductively Coupled Plasma (ICP) – Atomic Emission Spectroscopy (AES) after sample digestion	Ionization of sample then detection and quantification via emission spectrometry after suitable digestion step where any particulate iron oxides are converted to Fe ions	Dissolved Fe after digestion	100 mL (minimum size) sample bottle preserved with high purity nitric acid	7 µg/kg[25]	High detection limit of 7 µg/kg makes this method unsuitable for determining the concentration of iron corrosion products in power plants The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO_3)

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Inductively Coupled Plasma (ICP) – Mass Spectroscopy (MS)	Ionization of sample then detection and quantification via mass spectroscopy after suitable digestion step where any particulate iron oxides are converted to Fe ions	Dissolved Fe after digestion	100 mL (minimum size) sample bottle preserved with high purity nitric acid	1 µg/kg[26]	Suitable method for total iron corrosion products since detection limit less than optimal feedwater total iron value The optimum particulate iron digestion methodology is via the addition of acid to the sample combined with heating, e.g., using boiling nitric acid (HNO_3)
Corrosion Product Sampler sample collection (0.45 µm filter followed by ion exchange filter and known sample volume) followed by filter acid digestion, then analysis for determination of total mass of iron present on the filters. This value is then divided by the total volume of filtered sample to determine the average total iron value for the sampling period in µg/kg	Sample collection on 0.45 µm filter followed by an ion exchange filter at sample point operating pressure after sample cooling. Sample total filtered liquid volume recorded. Filters are then removed and digested. Total mass of iron on and in the filters determined via suitable dissolved iron analysis method such as ICP-MS, UV-Vis ferrozine method or AA. Total mass of iron is then divided by total sample volume to give average total iron concentration for the sampling period.	Total Fe	Plant operating pressure sample connection point downstream of a sample cooler. High pressure sample filter holder, high accuracy totalizing flow meter	As per iron analysis method selected	Optimal total iron corrosion products method with very low detection limit The optimum particulate filter and ion exchange filter iron digestion methodology is via the addition of acid to the sample combined with heating. Examples include thioglycolic acid ($CH_2(SH)COOH$) at 90 °C or boiling nitric acid (HNO_3)

Table 7: Summary of Analytical Methods for Copper

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
UV-Vis Spectroscopy	Neocuproine – a colorimetric method whereby Cu(I) reacts with 2,9-dimethyl-1,10-phenanthroline (neocuproine). This complex is than extracted with an organic solvent and the yellow color measured at a wavelength of 457 nm.	Dissolved copper, Cu, only as ions	200 mL (method needs 100 mL) neutral or acidic	Detection limit is 3 µg/L (1 cm cell)[27] 0.6 µg/L (5 cm cell)[31]	Method is unsuitable for determining the concentration of copper corrosion products in power plants due to it being a dissolved copper only method. Requires addition of digestion step **Method not accurate enough with 1 cm cell to be used in optimizing the reducing cycle chemistry in a power plant.**
UV-Vis Spectroscopy	Bathocuproine method. Colorimetric method where Cu(I) reacts with bathocuproine disulfonate (2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid, disodium salt). This complex is an orange-colored chelate and measured at 484 nm.	Dissolved Cu	100 mL (method needs 50 mL) neutral or acidic (pH 4-5 buffer)	20 µg/L – standard 5 cm cell[28]	Method is unsuitable for determining the concentration of copper corrosion products in power plants due to it being a dissolved copper only method. Requires addition of digestion step **Method not accurate enough with 5 cm cell to be used in optimizing the reducing cycle chemistry in a power plant.**

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Atomic Absorption (AA) Spectroscopy after sample digestion	Flame atomizer absorption spectrometry method after suitable digestion step where any particulate copper oxides are converted to Cu ions	Cu ions after particulate copper oxides are converted to Cu ions via a digestion step	100 mL high purity nitric acid preserved sample bottle (minimum sample bottle size)	1.5 µg/kg[29]	Suitable total copper corrosion products method with detection limit less than feedwater total copper value
Graphite Furnace Atomic Absorption (GF-AA) Spectroscopy after sample digestion	Graphite tube atomizer absorption spectrometry method after suitable digestion step where any particulate copper oxides are converted to Cu ions	Cu ions after particulate copper oxides are converted to Cu ions via a digestion step	100 mL high purity nitric acid preserved sample bottle (minimum sample bottle size)	0.014 µg/kg[34]	Suitable total copper corrosion products method with detection limit less than feedwater total copper value
Inductively Coupled Plasma (ICP) – Atomic Emission Spectroscopy (AES) after sample digestion	Ionization of sample then detection and quantification via emission spectrometry after suitable digestion step where any particulate copper oxides are converted to Cu ions	Cu ions after particulate copper oxides are converted to Cu ions via a digestion step	100 mL high purity nitric acid preserved sample bottle (minimum sample bottle size)	2 µg/kg[30]	Method has borderline suitability due to detection limit for total copper being the same as the feedwater total copper limit
Inductively Coupled Plasma (ICP) – Mass Spectroscopy (MS)	Ionization of sample then detection and quantification via mass spectroscopy after suitable digestion step where any particulate copper oxides are converted to Cu ions	Cu ions after particulate iron oxides are converted to Cu ions via a digestion step.	100 mL high purity nitric acid preserved sample bottle (minimum sample bottle size)	0.01 µg/kg[31]	Suitable total copper corrosion products method with detection limit less than feedwater total copper value

Analytical Method	Description	Analyte	Sample Collection Requirements	Best Reported Detection Limit	Comment
Corrosion Product Sampler sample collection (0.45 µm filter followed by ion exchange filter and known sample volume) followed by filter acid digestion, then analysis for determination of total mass of copper present on the filters. This value is then divided by the total volume of filtered sample to determine the average total copper value for the sampling period in µg/kg	Sample collection on 0.45 µm filter followed by an ion exchange filter at sample point operating pressure after sample cooling. Sample total filtered liquid volume recorded. Filters are then removed and digested. Total mass of copper on and in the filters determined via suitable dissolved copper analysis method such as, ICP-MS, or AA. Total mass of copper is then divided by total sample volume to give average total copper concentration for the sampling period.	Total Cu	Plant operating pressure sample connection point downstream of a sample cooler. High pressure sample filter holder, high accuracy totalizing flow meter	As per copper analysis method selected	Optimal total copper corrosion products method with very low detection limit The optimum particulate filter and ion exchange filter copper digestion methodology is with via the addition of acid to the sample combined with heating. Examples include thioglycolic acid ($CH_2(SH)COOH$) at 90 °C or boiling nitric acid (HNO_3)

10 Validation and Quality Control

A validation and quality control program is essential for successful corrosion product sampling and analysis. Figure 3 illustrates the process for obtaining an analysis result from a process stream.

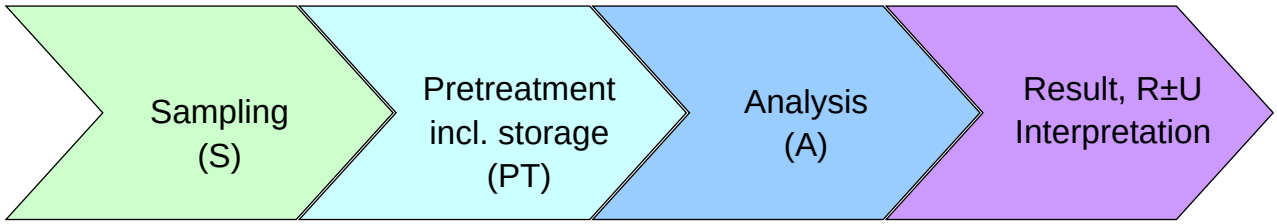

Figure 3: Steps of the sampling and analysis process. Pretreatment includes preservation, storage, digestion, etc.

A major focus of this TGD is obtaining a representative sample, i.e., minimizing the systematic error of the sampling step and selecting the appropriate analytical methodology. The next steps are equally important for obtaining a result that indicates the condition of the water-steam circuit. Random errors or systematic errors (bias) introduced in the pretreatment or analysis step may obscure the results and make the interpretation impossible or directly in error. Ideally, sampling must contribute the major part of the random variation of the final result, and the bias introduced through pretreatment and analysis must be marginal. Knowledge of the uncertainty associated with the result is also essential for the interpretation.

The trace levels associated with sampling and analysis of corrosion products make several sources of error likely, e.g.:

- Contamination from sample bottles used, chemicals added, or the surroundings when handling the sample
- Adsorption/desorption effects when inadequate container material is used
- Improper division of samples containing low amounts of particles and leading to large random errors.

The purpose of the validation is to document that the analysis is fit for purpose, i.e., that all the methods of pretreatment and analysis work satisfactorily and do not introduce major errors. The purpose of the quality control (QC) during application of the methods is to keep the quality at the level demonstrated by the validation and avoid errors that diminish the quality of the data. These two tools together lead to a good estimate of the uncertainty of the result.

The advice on validation and QC given here is on a general level, focusing on the principles and the main quality parameters. The example of a validation program described below is on the verification level that is usually sufficient when a well-known (or standardized) method that has previously been validated is applied in a specific laboratory. Guidance on the experimental design and statistical processing is available in specialized literature (e.g., the Eurachem Guide[32]), and the program should be adjusted considering the analytical method applied.

As a starting point, the expectations of the analysis must be considered. Stating the expectations as specifications typically for accuracy, reproducibility, detection limit and uncertainty provides a framework for the validation and greatly helps to evaluate the outcome.

The measurements during the validation of a method should be performed using the operating procedures of the method and the related laboratory tasks (e.g., cleaning and rinsing of glass and plastic ware); i.e., everything should proceed as intended for routine analysis.

10.1 Validation of the Analytical Method

The main quality parameters to test for the analytical method are:

- Linearity over the relevant measuring range
- Accuracy – this is a measure of the systematic error
- Repeatability over the measuring range – this is a measure of the random variation when measurements are performed within short time intervals under otherwise constant conditions.
- Reproducibility at selected levels – this is a measure of the random variation taking into account the small contributions to errors that vary from batch to batch of samples (e.g., laboratory conditions such as humidity and temperature, calibration, background levels in ultrapure water and chemicals, operator skill).
- Detection limit – describes the lowest measurable concentration that is statistically different from zero.

The first three of these quality parameters may be estimated by means of a linearity experiment in which a set of independent standards distributed across the measuring range are analyzed under repeatable conditions.

Example: Prepare six to eight standards with concentrations spanning the relevant measuring range (may be less than the measuring range of the instrumental method). The concentrations should be more closely spaced in the low end (e.g., using the 1, 2, 5, 10 sequence) and then gradually become equidistant in the high end. The standards should be prepared from a source independent of the calibration standards of the instrumental method, e.g., by using stock solutions from two different suppliers. Analyze four or five different aliquots of each standard in random order.

The linearity is estimated from a plot of the measured concentrations versus the nominal concentrations. This relationship between measured and nominal concentration is estimated by means of linear regression. It should be essentially linear as indicated by the correlation coefficient (i.e., $R^2 > 0.99$).

The accuracy is evaluated by comparing the slope of the regression line with the ideal value 1.00. The slope should match this value within the specification of accuracy (e.g., 1.00 ± 0.02). Ideally, the intercept of the regression line should be close to zero. If this is not the case,

background values in the ultrapure water or in the chemicals may explain a positive value, and a correction term may be applied.

The repeatability across the measuring range is evaluated by plotting the standard deviation of the results for each standard versus the nominal concentration. This will often show that the repeatability is approximately constant up to a certain level and then increases with concentration above that level. The same behavior is likely for the reproducibility and in turn for the uncertainty of the result.

The reproducibility is evaluated by analyzing standards at selected levels over periods of several days to allow for batch to batch (or day to day) variation. The standard deviation of these results is used as a first estimate of the random variation contributing to the uncertainty of results produced in routine analysis.

Example: Prepare standards at four concentrations, two at the low end of the measuring range, one in the middle, and one at the high end. The two low concentrations may be selected according to the level expected in the real samples. The standards should be prepared independently of the calibration standards used in the analysis. A subset of these standards are analyzed over eight to ten batches covering a period of, for example, two weeks. The standards should be analyzed in random order, and preferably mixed with other samples.

From the results, the mean value and reproducibility standard deviation are calculated and compared with the nominal concentration and the repeatability standard deviation, respectively.

The detection limit is estimated by repeated measurements on blank samples or standards with concentration slightly above the expected detection limit.

Example: Prepare a blind sample of ultrapure water and a standard with concentration at the lowest level expected to be measured. Analyze eight to ten aliquots of each in random order under nominally identical conditions.

From the results calculate the mean value and the standard deviation. The standard deviation could be compared to the value obtained by extrapolation of the plot of repeatability standard deviation versus nominal concentration described above. From these data a standard deviation near the detection limit, s_0, is estimated. The actual detection limit is often calculated as $3*s_0$. At this level the uncertainty on a single measurement from random variations is around 100 %. At $6*s_0$ the uncertainty is around 50 %, and at $10*s_0$ it is around 30 %. The limit of quantification should be set somewhere in that range according to the acceptable uncertainty. It is advisable to analyze a real standard in that range to verify experimentally that samples at the quantification limit can be reasonably measured.

10.2 Validation of the Complete Method

Validation of the complete method including the pretreatment steps may be approached in a stepwise fashion:

- Pass three or four samples of ultrapure water and two standards of low concentration through the pretreatment and analyze them in random order. Check that the mean values are at the expected level, and that the standard deviations are comparable to the repeatability standard deviation of the analytical method. This is a basic check for contamination and adsorption effects.
- Obtain a set of real samples that may be assumed to be equal. Pick the samples during a period of steady load (as recommended earlier), use a sampling point of importance, e.g., feedwater, and establish the optimal sampling conditions according to Section 5 of this TGD. Take 15 or 18 samples in rapid order. Randomize the order of the samples and divide them into three batches of five or six samples. Pass each batch through pretreatment and analysis on three different days covering the maximum storage (and/or transportation) time. Review the results and discard obvious outliers – experience shows that a few samples in such a group may occasionally contain much higher concentrations than the others due to their particulate constituent. Calculate the mean value and standard deviation for each batch and compare. Both parameters should be comparable among the three batches if the pretreatment works as expected. The standard deviations give an impression of the random variation of the sampling process; they are most likely higher than the reproducibility standard deviation.
- Comparing the estimated accuracy of the complete analysis with that of another laboratory or with that of an independent analysis method is indispensable. The laboratory used for comparison should be experienced in the field and have a working quality management system, e.g., according to the standard ISO 17025.
  Obtain a set of 10-12 real samples under ideal sampling conditions as described above, randomize the order, and split the samples in two batches. One batch is analyzed by means of the method under test, and the other is analyzed by the other laboratory (or method). The results are reviewed and obvious outliers removed. Means and standard deviations for the two batches should be comparable, meaning that the sampling process is the main contributor to the random variation. If the mean values deviate more than 20 % or so, there is reason to look for a systematic error somewhere.

Certified reference materials (CRMs – samples of items to be tested with guaranteed levels of constituents) are frequently used for validation purposes. However, for analysis of corrosion products, it is unlikely that certified reference materials matching the samples are commercially available. For methods that give (or approximate) total content, it may be worthwhile to analyze a CRM of, for example, drinking water with concentration in the same range as the real samples. Obtaining the certified concentration demonstrates that pretreatment and analysis essentially work correctly and it may be assumed to be the case for the real samples also.

The results of the validation should be summarized in a report stating the main findings for the quality parameters and the evaluation according to the specifications of the analysis.

10.3 Quality Control

The internal quality control performed during routine analysis is the main tool for maintaining quality and ensuring that the analysis is well controlled.

The correct functioning of pretreatment and analysis may be checked through measures such as:

- Running a couple of QC standards with every batch of samples. The QC standards should be prepared independently of the calibration standards of the instrumental method. The concentrations of the QC standards should be chosen at levels where the reproducibility standard deviation is known, i.e., slightly above the typical range of results and at the level of occasional high results. Record the results of the measurements on the QC standards on control charts (X-chart for the mean, see Nordtest TR 569[33] and ISO 8258[34]), since this tool makes it easy to spot trends signaling systematic errors and allows calculation of standard deviations comparable to the reproducibility standard deviation.
- Routinely, e.g., two to four times per month, running blind samples through the analysis and accumulating the results on a control chart. This will indicate any contamination of ultrapure water, chemicals, reused glass and plastic, etc.

The random variation in the sampling process may be checked at selected key sampling points by routinely taking three samples within a short time when steady-state conditions of the sampling systems may be assumed. The standard deviation is calculated for each set of samples and pooled over several rounds to give an estimate of the standard deviation attributed to the complete process. In such a data set, obvious outliers are likely to appear, and they may be discarded prior to calculating the standard deviation. Values that are not clear outliers should be included in the calculation.

Inter-laboratory comparison is a strong tool for quality control, and it is strongly recommended to arrange or take part in such a comparison two or three times per year. It is essential to take the samples under steady sampling conditions and to randomize the sample order before splitting into batches. At least five samples per batch are recommended in order to be able to identify outliers in the results. This setup may be readily extended to three or four participating laboratories without the effort to arrange and evaluate the comparison becoming unmanageable. With more participating laboratories the number of samples per batch may be reduced to three or four.

The strength of inter-laboratory comparison increases with the number of participating laboratories. A larger group of laboratories may agree to cooperate for the common benefit by arranging round robins (also known as proficiency tests) in which realistic samples supposed to be equal are distributed to the laboratories. The samples are analyzed and the results submitted and processed centrally, e.g., according to the standard ISO 5725-2. However, the effort to arrange a round robin, to prepare samples and test their homogeneity, to process the data and to report the results is large, and an agreement on management resources will most likely be made within the group.

Whenever a deviation occurs in the quality control, follow-up measures must be taken to find the cause, correct the problem and demonstrate that the analysis is back under control.

Periodic evaluation of the outcome is an important part of running a quality control scheme. At the evaluation, the control charts should be reviewed for trends and the standard deviations and mean values should be compared with values from previous periods and validations. Accumulation of this experience builds up good estimates of reproducibility and bias for the laboratory that may be attributed to the pretreatment and analysis process, and the uncertainty from these sources for a single sample may then be expressed by Eq. (4):

$$U = 2\sqrt{b^2 + s_r^2} \qquad (4)$$

Here, U is the uncertainty at approximately the 95 % confidence level, b is a (small) bias that may be present, and s_r is the reproducibility standard deviation.

The magnitude of the uncertainty inherent in the sampling may be estimated by gathering data from quality control measurements for selected sampling points and from inter-laboratory comparison. Other methods to estimate the uncertainty from sampling are described in Nordtest TR 604.[35] It is understood that the uncertainty stated by the laboratory covers the pretreatment and analysis steps.

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