

Sampling for Chemical Control – Pitfalls and Compromises

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Sampling from a water /steam circuit

- The Chemistry of water and steam in a high temperature circuit can only be fully controlled if the composition is known.
- Sampling systems are needed to convey solutions from the operating circuit at high temperature and pressure to the analytical equipment at controlled low temperature and at atmospheric pressure with **minimal** change.
- THE PITFALLS:
 - Errors that result from deposition in sample lines.
 - Errors that result from chemical reactions in sample lines.
 - Unrepresentative sampling in two-phase conditions.
 - Errors that result from release of materials from sample lines.

ISO Standard 5667-7

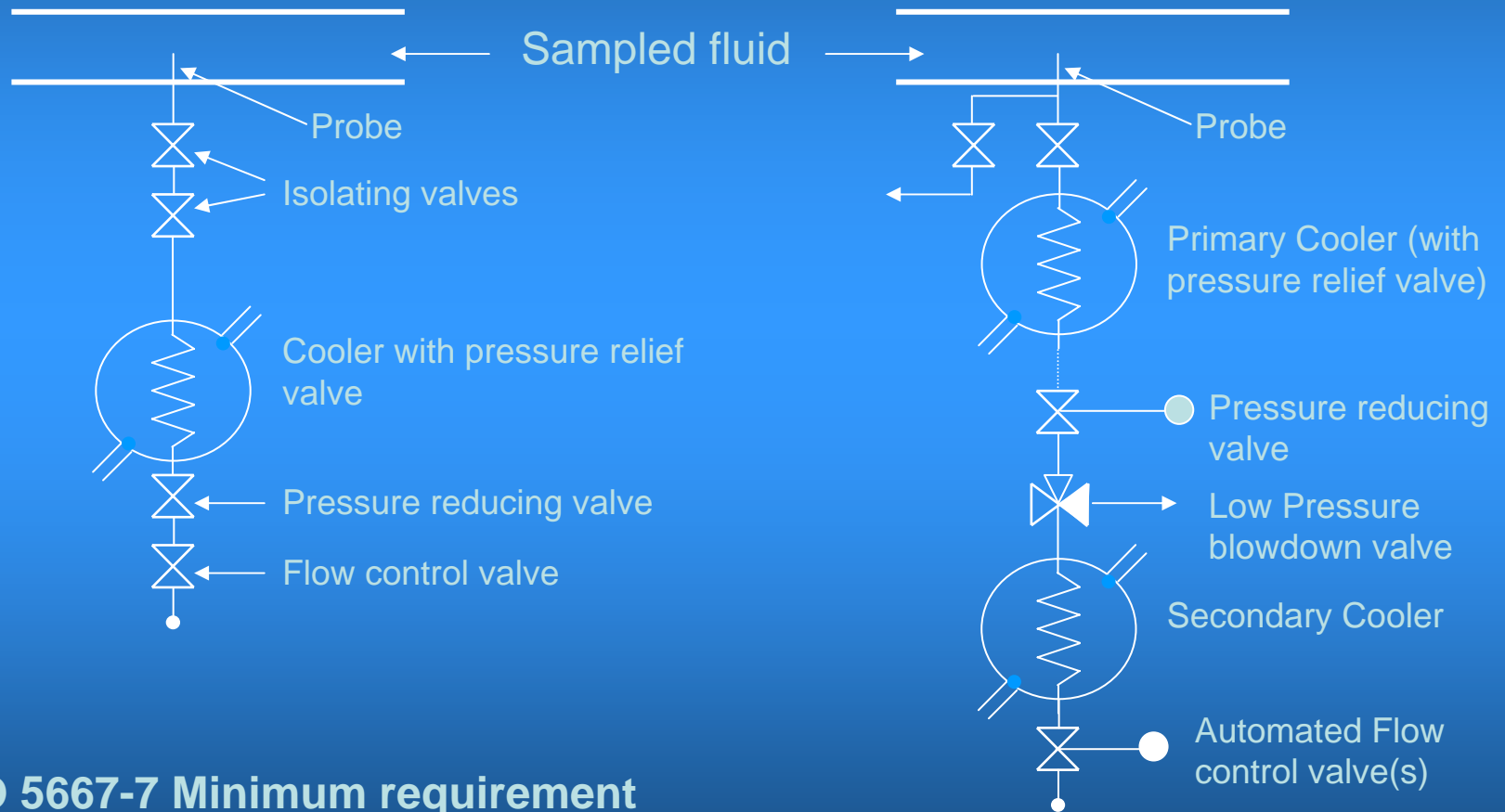
- ISO Standard 5667-7:1993.

Water Quality – Part 6: Sampling

Section 6.7 “Guidance on Sampling of Water and Steam in Boiler Plants”

This Standard is Currently Under Revision but is nonetheless a good source of advice.

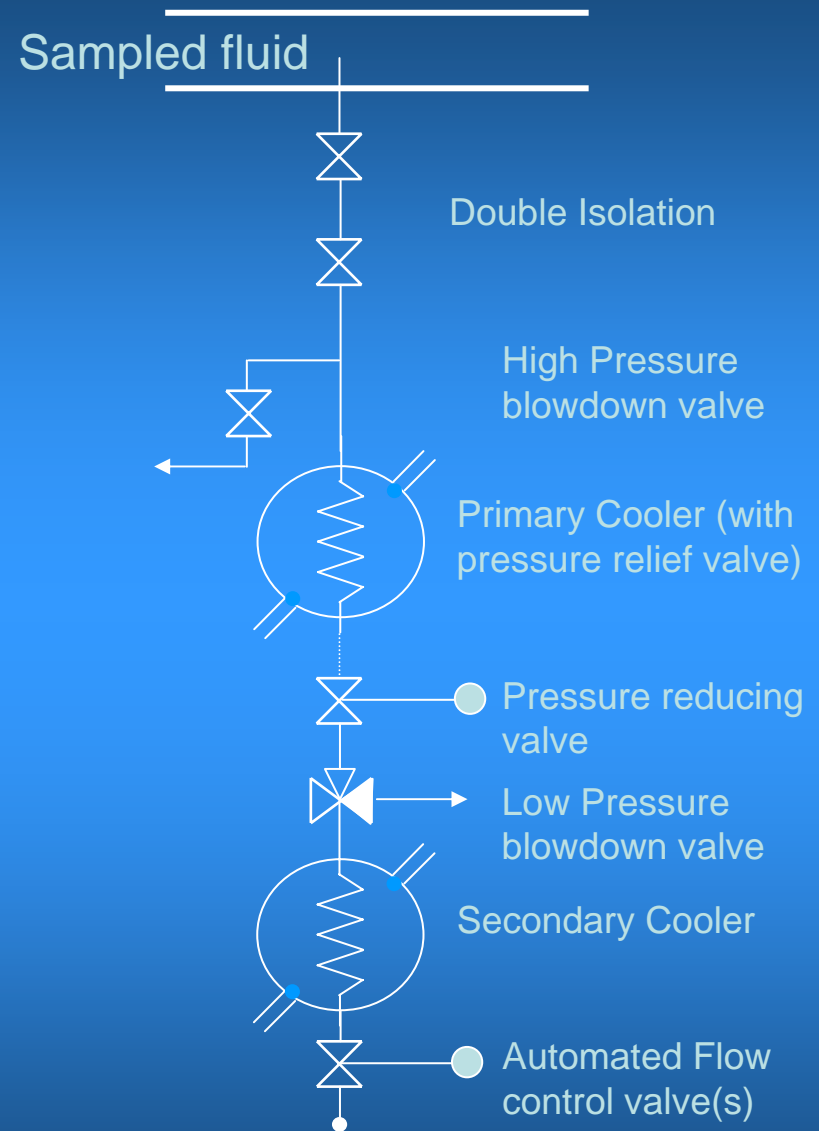
The minimum requirement of the Standard may be less than the optimum



ISO 5667-7 Minimum requirement

Sampling system must be safe and maintainable

- Double isolation,
- Flow cut-off on high temperature,
- Address risk of over-pressurisation of coolers,
- Pressure reducing valve must be serviceable,
- Flow control should respond to changes in system pressure.



The sampling probe

- When sampling for pH and conductivity measurements it is merely necessary to ensure that the probe withdraws a sample from the bulk flow.
- When sampling for total iron, total copper, etc. (i.e. particulates of similar density to the fluid) the probe must face into the flow.
- When sampling for droplets in steam (i.e. large density difference) it is essential to use an iso-kinetic sampling probe and to match the sample line flow velocity to the process flow.

Sample line flow rate

- For parameters such as total iron, total copper, etc. it is important to keep the flow turbulent to keep the particulate material in suspension.
 - ISO Standard 5667-7:1993. states: “Use pipework of sufficiently small bore to ensure that the sample is transported under turbulent flow conditions with Reynolds Number $>4,000$.”
 - ASME Handbook of Water Technology for Thermal Power Systems states: “When sampling water, the velocity in the sampling line should be kept great enough to produce a Reynolds Number of at least 20,000.”

Reynolds Number Criteria

- The wide range of published criteria had been rationalised by Daucik (PowerPlant Chem. 11(7), 2009) who recognised that the critical Reynolds number to ensure turbulent flow in a tube is a function both of tube bore, d , and bend or coil diameter, D :

$$Re_{\text{Crit}} = 2300 \times \left\{ 1 + 8.6 \left[\frac{d}{D} \right]^{0.45} \right\}$$

- I.e. for a straight tube it is merely necessary to achieve $Re_L > 2,300$, but in a cooling coil it is essential to achieve a much higher value ($Re_L > 12,000$ or more).

Sample line flow rate

- **Srisukvatananan, Lister, Svoboda and Daucik**

“Assessment of the state of the art of sampling of corrosion products from water/steam cycles “

PowerPlant Chemistry 2007, Vol 9(10) pp 613-626:

“Sampling velocity is a key parameter. It has been reported that sampling velocity is a critical factor controlling deposition and erosion on sample tube walls.....Velocities near 1.8 m.s^{-1} (6 ft.s^{-1}) seem optimum but other velocities can provide acceptable results.”

A Practical Sampling Line

$$Re_L = \frac{\rho \cdot V \cdot L}{\mu}$$

- DN6 Schedule 80

Internal diameter	Mass flow rate	Temp.	ρ	Volume flow rate	V	μ	Re_L
mm	kg.h ⁻¹	deg C	kg.m ⁻³	m ³ .s ⁻¹	m.s ⁻¹	Pa.s	
5.47	60	300	715.3	2.33 $\times 10^{-5}$	0.991	9.06 $\times 10^{-5}$	42833
		200	870.9	1.91 $\times 10^{-5}$	0.814	1.36 $\times 10^{-4}$	28441
		100	962.9	1.73 $\times 10^{-5}$	0.737	2.84 $\times 10^{-4}$	13640
		50	992.3	1.68 $\times 10^{-5}$	0.715	5.49 $\times 10^{-4}$	7071
		25	1004.0	1.66 $\times 10^{-5}$	0.706	8.97 $\times 10^{-4}$	4324

Is this too low?

Or is this about right?

The consequences of not using the right sample line flow

- Particles may settle out, giving erroneous (low) total iron or total copper.
- Pre-deposited material may be stripped out on increasing the flow, giving erroneous (high) values.
- For sampling from two phase flows, the only correct sample flow rate is that which gives the iso-kinetic sampling condition. Deviation from this condition will always introduce errors.

Sample line cooling

- The heat to be abstracted from a sample is directly proportional to the mass flow rate and the enthalpy of the sampled fluid.
- In some cases the costs (mainly heat loss from the system over operating life) exceed the installation cost.
- Strong economic justification for getting the design right.

Heat to be extracted

Internal diameter	Mass flow rate	Temp.	ρ	Enthalpy to be extracted	Cooling load
mm	kg.h ⁻¹	deg C	kg.m ⁻³	kJ.kg ⁻¹	kW
5.47	60	560 SH steam	46	3347	56
		340 Sat steam	102.4	2502	41.7
		340 Boiler water	618.7	1467	24.4
		150 Feed water	925.6	522	8.7

The role of the primary cooler

- Since many reactions can continue as long as hot water passes along the sample line it can be beneficial to cool the sample as soon as possible after extraction from the process water.
 - Examples:
 - Oxygen reacts with hydrazine and other scavengers on hot magnetite covered steel surfaces.
 - Oxygen may react with pre-existing oxides in sample lines.
 - Dissolved copper can react with steel giving enhanced iron concentration and depleted copper concentration.
 - These all give double false results at the analysis panel.
- The longer the sample line, the greater is the scope for error.

The role of the secondary cooler

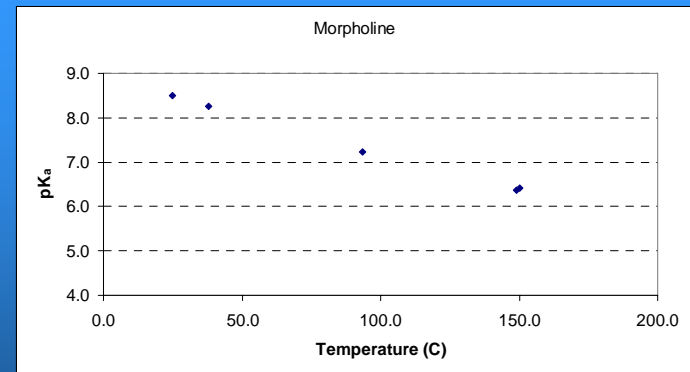
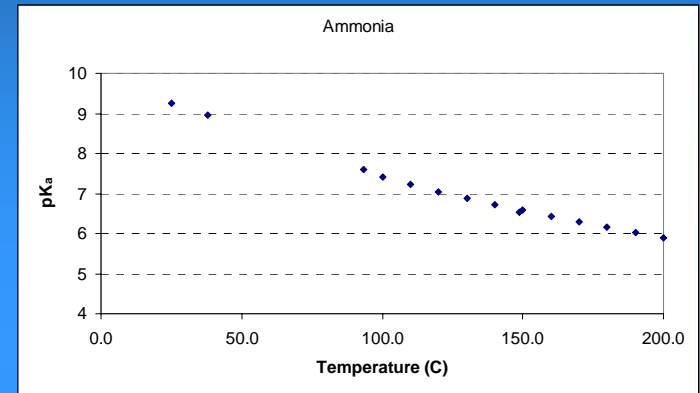
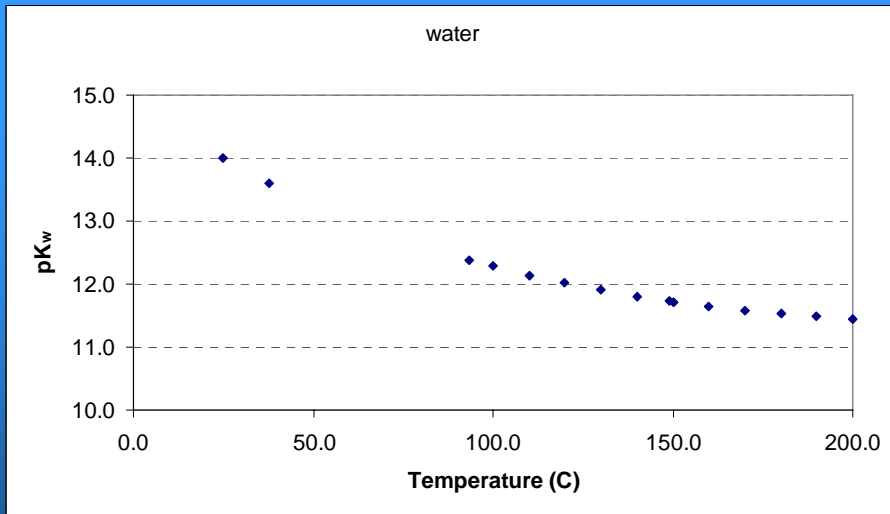
- Many modern instruments (particularly pH and conductivity) detect the temperature of the sample and correct back to 25°C.
- The closer the approach of actual temperature to 25°C the less reliance there is on instrumental correction.
- Many key processes have different temperature dependencies.

Temperature dependency examples

Nernst equation:

$$E = E^{\circ} - (RT/zF) \cdot \ln \{f [c]\}$$

Equivalent conductivity of each ion also varies with temperature.



The Temperature Correction Pitfall

- Automatic temperature correction can only give the correct answer if it is set up for the chemical system that is being measured.
- Temperature dependence of the properties of, say, feedwater will not be the same as the temperature dependence of standard solutions (buffers, etc.).
- The closer that the sample is to 25°C the smaller the potential error becomes.

The Pressure Drop Pitfall

- To drop pressure the sample must flow through a constriction.
 - Acceleration and deceleration are inevitable.
 - Electrokinetic effects can stimulate electrode reactions in the acceleration and deceleration regions.
 - Those reactions can, in severe cases, include oxygen evolution, and can yield false high values at the downstream instrument.
- The best designs of pressure reducing valves minimise (but may not totally prevent) such errors.

Concluding Summary

- The values of chemical concentrations and related parameters that we measure at a sampling panel will seldom be exactly the same as the values in the process.
- The best compromises are achieved by:
 - Optimising the flow rate,
 - Suppressing reactions in sample lines by rapid cooling and minimising line length,
 - Minimising the need for instrumental temperature compensation,
 - Using pressure reducing equipment that minimises the error risk from electrokinetic effects.

Thank you for your attention

- Any questions?