EDXRF Analysis of Corrosion Residues in Cooling Water Systems of Nuclear Power Plants

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OVERVIEW

Objective: analysis of corrosion residues in the water-cooling system of nuclear power plants
Methods: Energy Dispersive X-Ray Fluorescence
Results: Simple and effective water filter analysis

One of the safety aspects in nuclear power plants (boiling water reactor and pressurized water reactor) is the early detection of corrosion of the metal alloy components of the cooling system. The corrosion residues in the cooling water are an early indication of a safety problem. Direct determination of metals in cooling water is not possible due to very low concentrations. Therefore, filters are placed in the cooling system to collect corrosion residue over time. Typically, a volume of 100 liters of cooling water passes through the filter.

Two types of filters are used:

- Cellulose-based "normal" filters for secondary circuit of pressurized water reactors (PWR)
- Ion exchange filters for primary circuit in boiling water reactors (BWR) and in PWR

Elements of interest:

- Cations: Fe, Co, Cr, Cu, Mn, Ni and Zn. Also Pb, Ca, Mg, Na and Cs.
- Anions: I, Cl and Br.

Generally, these filters are analyzed by ICP-OES and must therefore be put into solution before analysis. The analysis time, including the preparation of samples, easily takes half a day. This method also requires the use of hazardous chemicals.

METHODS

Sample preparation

The EDXRF analysis does not require sample preparation. The filter is put into the instrument directly. The scan takes less than 10 minutes per filter. The analysis is non-destructive, which keeps the sample for future reference. The calibration of the instrument is straightforward, and the long-term stability is excellent.

Analysis with ARL QUANT'X EDXRF Spectrometer

The Thermo Scientific™ ARL™ QUANT'X is a direct-excitation benchtop EDXRF spectrometer with 9 filters and a 50-Watt X-ray tube (Rh or Ag target). This instrument allows for the analysis of fluorine to uranium in the analytical range of ppm levels to high percent.

All types of samples can be analyzed: solids, powders, liquids, filters and thin layers with analysis in air atmosphere, vacuum or helium. The new silicon drift detector (SDD) with high-transmission window permits an excellent detection of the various elements that are deposited on the filter. The SDD is cooled by Peltier effect and its large effective area of 30 mm2 permits three times faster analysis compared to older detector types.

Figure 1. ARL QUANT'X EDXRF ANALYZER

Sample characteristics on filters

- Low amount of corrosion material on the filter
- Filters with a diameter of 47 mm, possibly with a non-homogeneous distribution of the sample

Specific benefits of ARL QUANT'X

- Direct excitation ensures that all primary radiation is used to excite the sample
- The new SDD detector allows excellent detection efficiency for all elements
- Large area of excitement allowing a representative analysis of the filter

Quantitative Analysis – Reference Materials

Preparing reference materials in the laboratory or from third-party suppliers:

- Cellulose-based filters are made by passing a watery suspension of solid metal oxides through the filters
- Ion exchange filters are prepared by passing a solution containing soluble metals through the membranes.

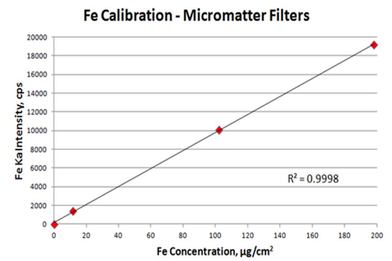
RESULTS

Example 1: Iron Determination

Determining iron deposits extracted from the secondary water-cooling system of a PWR on cellulose filters.

Calibration on Micromatter filters at three different concentrations, including one white filter (Figure 2). Validation compared to ICP-OES (Figure 3).

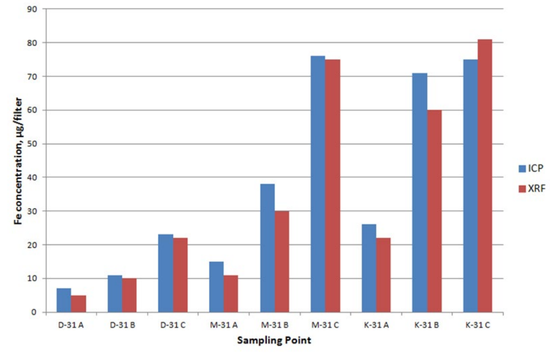
Figure 2. Determination of Fe - Calibration



Condition parameters

30 kV
Filtre Pd
Air
30 S

Figure 3. Determination of Fe - Validation



Example 2: Ion exchange filters

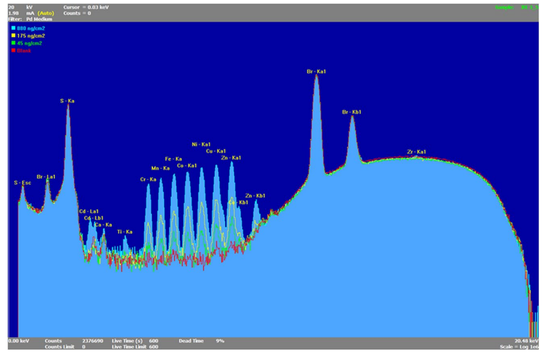
Filters containing Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, U and Cd are analyzed using an ARL QUANT'X EDXRF with direct excitation using primary filters, SDD detector, 50W X-ray tube with Rh anode.

The analysis method is optimized by combining the best analysis conditions for each portion of the periodic table of elements. Measurement times depend on the load on the filter and are chosen between 60 seconds and 240 seconds per condition.

Table 1. Conditions

Condition	Filter	Voltage (kV)	Atmosphere	Elements
Low Za	None	4	Vacuum	Al
Mid Za	Thick Pd	16	Vacuum	Cr, Mn, Fe, Co, Ni
Mid Zb	Medium Pd	20	Vacuum	Cu, Zn
Mid Zc	Thick Pd	28	Vacuum	Zr, U
High Za	Thin Cu	40	Vacuum	U, Cd

Figure 4. Filter spectra with different loads of material



The total load of material on an ion exchange filter is rather low, hence a simple linear calibration curve is sufficient in most cases and provide an $R^2 > 0.999$ and excellent repeatability and reproducibility. The filters contain Br of which the K lines interfere with U L lines.

Detection limits

The detection limits below are calculated using a white filter.

Table 2. Detection limits in ng/cm² with 60 seconds of analysis per condition

Minimum Detection Limits (MDLs), ng/cm²										
Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	Cd	U*
Ka	*Ka*	*Ka*	*Ka*	*Ka*	*Ka*	*Ka*	*Ka*	*Ka*	*Ka*	*Lb*
17	**6**	**18**	**13**	**10**	**13**	**5**	**11**	**23**	**85**	**195**

* Br Kb interferes with U La hence the higher MDL

CONCLUSION

EDXRF analysis provides an effective tool to monitor corrosion of the cooling system in the nuclear industry by analysis of water filters.

- Analysis of the filters is non-destructive
- No sample preparation is required
- Calibration and analysis are fast and simple
- The entire filter is analyzed, which avoids problems due to sampling inhomogeneities
- Detection limits are excellent, allowing for short analysis times
- The SDD detector cooled by Peltier effect also allows the detection of radioactive elements.

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