Designation: D6502 – 10 (Reapproved 2022)

Standard Test Method for Measurement of On-line Integrated Samples of Low Level Suspended Solids and Ionic Solids in Process Water by X-Ray Fluorescence (XRF)[1]

This standard is issued under the fixed designation D6502; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the operation, calibration, and data interpretation for an on-line corrosion product (metals) monitoring system. The monitoring system is based on x-ray fluorescence (XRF) analysis of metals contained on membrane filters (for suspended solids) or resin membranes (for ionic solids). Since the XRF detector is sensitive to a range of emission energy, this test method is applicable to simultaneous monitoring of the concentration levels of several metals including titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, mercury, lead, and others in a flowing sample. A detection limit below 1 ppb can be achieved for most metals.

1.2 This test method includes a description of the equipment comprising the on-line metals monitoring system, as well as, operational procedures and system specifications.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Flowing Process Streams
D3864 Guide for On-Line Monitoring Systems for Water Analysis
D4453 Practice for Handling of High Purity Water Samples
D5540 Practice for Flow Control and Temperature Control for On-Line Water Sampling and Analysis
D6301 Practice for Collection of On-Line Composite Samples of Suspended Solids and Ionic Solids in Process Water

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of other terms used in this standard, refer to Terminology D1129 and Guide D3864.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *emission intensity, n*—the measure of the amplitude of fluorescence emitted by a sample element.

3.2.1.1 *Discussion*—This measurement is correlated with a calibration curve for quantitative analysis. The emission intensity generally is given in units of counts per second (c/s).

3.2.2 *excitation source, n*—the component of the XRF spectrometer, providing the high-energy radiation used to excite the elemental constituents of a sample, leading to the subsequent measured fluorescence.

3.2.2.1 *Discussion*—The excitation source may be an electronic x-ray generating tube or one of a variety of radioisotopes emitting an x-ray line of a suitable energy for the analysis at hand.

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2.3 *integrated sample, n*—the type of sample collected by concentrating the metal constituents of a water sample using a filter or an ion-exchange resin.

3.2.3.1 *Discussion*—These samples typically are collected over long time periods (up to several days). The result of analysis of the collection medium yields a single measurement, which, when divided by the total sample volume, is interpreted as the average metals concentration during the time of collection.

3.2.4 *ionic solids, n*—matter that will pass through a 0.45 µm filter and may be captured on anion or cation ion-exchange membranes, or both.

3.2.5 *suspended solids, n*—matter that is removed by a 0.45 µm filter.

3.2.6 *x-ray fluorescence (XRF) spectroscopy, n*—an analytical technique in which sample elements are irradiated by a high-energy source to induce a transition from the ground state to an excited state.

3.2.6.1 *Discussion*—The excitation source is in the 5 KeV to 50 KeV x-ray range. The resulting transition elevates an inner-shell electron to one of several outer shells. The excited state is unstable and those excited elements will spontaneously drop back to their ground state with a concurrent emission of fluorescent radiation. The energy (or wavelength) of the fluorescence is unique for each element, so the position of the emission lines on the energy scale serves to identify the element(s). Then, the intensity of an emission peak may be used, with proper calibration methods, to determine the concentration of an element in the sample.

3.3 *Acronyms:*

3.3.1 *EDXRF, n*—energy-dispersive x-ray fluorescence

3.3.2 *WDXRF, n*—wavelength-dispersive x-ray fluorescence

4. Summary of Test Method

4.1 The concentrations of particulate, or dissolved metals, or both, in water streams are determined through accumulation on appropriate collection media (filters or ion exchange materials) and detection by x-ray fluorescence spectroscopy, providing real time determination of iron and other metals found in water streams. The water sample delivered into the monitoring system passes through a flow sensor, and then, to a flow cell assembly containing a membrane or resin filter, depending on the application of interest. For an application where only dissolved metals are to be analyzed, the sample needs to be filtered upstream of the sample chamber to prevent particulate contamination of the resin membrane surface. A sample bypass valve is used for flow control through the sample chamber. Two sample chambers in sequence can be used to determine both particulate and dissolved components of the metal(s) of interest. X-ray fluorescence is used to determine the concentration of the captured material. XRF analysis gives a measure of total elemental concentration independent of the oxidation state or molecular configuration of the element. Elements with atomic numbers 13 through 92 can be detected.

4.2 The filter chamber is essentially a variation of the traditional corrosion product sampler used to collect integrated samples (see Practice D6301). The main difference in the design of the flow cell in the on-line monitor is that the sample enters the filter chamber in a way that allows an x-ray probe to be positioned in close proximity to the filter or resin membrane surface.

4.3 Since even a small quantity of water covering a sample significantly attenuates both the excitation and emission radiation, a computer controlled valve switching system is incorporated into the monitor. In one position, this valve allows sample flow to proceed through the monitoring unit and metals to accumulate on the filter or resin membrane while the flow total is monitored. In the other position, the valve introduces air or other gas to purge the filter chamber of liquid while the sample is diverted to drain. It is during the air purge that the x-ray measurement takes place. In this way, the monitor operates by continuously alternating between two modes: a sample accumulation mode and an analysis mode. Typical time assignments for these modes for sample concentrations in the low ppb range are five minutes each; thus, in one cycle, sample accumulates for five minutes followed by a five minute x-ray measurement. With various delays for valve switching operations, computer extraction of x-ray data, and date manipulation, the measurement cycle in this case lasts approximately 14 minutes. Sample accumulation and analysis times are program variables, which may be adjusted prior to each monitoring session. A monitoring session typically lasts several days for high purity water such as secondary feedwater for nuclear steam generators.

5. Significance and Use

5.1 Corrosion products, in the form of particulate and dissolved metals, in the steam and water circuits of electricity generating plants are of great concern to power plant operators. Aside from indicating the extent of corrosion occurring in the plant, the presence of corrosion products has deleterious effects on plant integrity and efficiency. Deposited corrosion products provide sites at which chemicals, which are innocuous at low levels, may concentrate to corrosive levels and initiate under-deposit corrosion. Also, corrosion products in feedwater enter the steam generating components where deposition on heat transfer surfaces reduces the overall efficiency of the plant.

5.2 Most plants perform some type of corrosion product monitoring. The most common method is to sample for long time periods, up to several days, after which laboratory analysis of the collected sample gives the average corrosion product level over the collection time period. This methodology is referred to as integrated sampling. With the more frequent measurements in the on-line monitor, a time profile of corrosion product transport is obtained. Transient high corrosion product levels can be detected and measured, which cannot be accomplished with integrated sampling techniques. With this newly available data, plant operators may begin to correlate periods of high corrosion product levels with controllable plant operating events. In this way, operators may make more informed operational decisions with respect to corrosion product generation and transport.