Designation: D 6502 – 99

Standard Test Method for On-Line Measurement of Low Level Particulate and Dissolved Metals in Water by X-Ray Fluorescence (XRF)[1]

This standard is issued under the fixed designation D 6502; 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 particulate forms) or resin membranes (for dissolved forms). 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 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]
D 1129 Terminology Relating to Water[2]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]
D 3370 Practices for Sampling Water from Closed Conduits[2]
D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis[2]
D 4453 Practice for Handling Ultra-Pure Water Samples[2]
D 5540 Practice for Flow Control and Temperature Control for On-Line Water Sampling and Analysis[2]
D 6301 Practice for Collection of Samples of Filterable and Nonfilterable Matter in Water[2]

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D 1129 and Practice D 3864.

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. 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, which provides the high energy radiation used to excite the elemental constituents of a sample leading to the subsequent fluorescence which is measured. The excitation source may be an electronic x-ray generating tube or one of a variety of radioisotopes which emit an x-ray line of a suitable energy for the analysis at hand.

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. 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 *x-ray fluorescence (XRF) spectroscopy*, *n*—an analytical technique in which sample elements are irradiated by a high energy source which induces a transition from the ground state to an excited state condition. Using an excitation source in the 5 to 50 KeV x-ray range, the resulting transition elevates an inner shell electron to one of several outer shells. The excited state condition is unstable and elements so excited 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

---

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-formed Deposits and Surveillance of Water.

Current edition approved Dec. 10, 1999. Published March 2000.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

used, with proper calibration methods, to determine the concentration of an element in the sample.

3.3 *Symbols*:

3.3.1 WDXRF = Wavelength Dispersive X-ray Fluorescence

3.3.2 EDXRF = Energy 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 D 6301). 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.

6. Interferences

6.1 *Coincidence of Certain Emission Lines*—In XRF, each element emits fluorescence at characteristic wavelengths which makes element identification unambiguous; however, certain pairs of emission lines from different elements occur sufficiently close in energy that the resulting overlap causes difficulties in quantitative analysis. An example of this is the Kα line of cobalt, which occurs at 6.925 keV (average) and the Kβ line of iron, which occurs at 7.059 keV (average). In the case of a small amount of cobalt in the presence of a large amount of iron, which is a typical case among corrosion product samples from steam generating plants, the cobalt analysis is hindered by the iron in the sample. Note that iron is not similarly affected by the presence of cobalt since the iron Kα line may be isolated to extract iron emission intensity.

6.1.1 There are three strategies which may be used to ameliorate the type of interference described above. First, the ratio of Kα to Kβ emission intensity is constant and known for each element; thus, from a higher than expected intensity of iron Kβ emission, relative to the Kα emission, the presence of cobalt may be inferred and measured. Second, the use of a cryogenically cooled, solid-state detector greatly improves the resolution (by reducing the band width of individual emission peaks) such that direct measurement of cobalt is possible. Third, the use of wavelength dispersive XRF (WDXRF) instrumentation provides the optimum line separation; however, WDXRF instrumentation is much more expensive, and less robust for on-line use, than energy dispersive XRF (EDXRF) spectrometers.

7. Apparatus

7.1 The on-line metals analyzer[3] consists of the following main components: x-ray probe and associated electronics, flow cell and filter chamber, flow totalizer, valve switching system, and instrument control and data acquisition system.

7.2 The volume of sample delivered to the flow cell assembly is monitored using a flow totalizer. Several varieties of these are available including piston, turbine, and Coriolis types. The flow totalizer should have capability for computer communication.

7.3 The water sample is passed through a specially designed filter chamber containing a membrane filter (typically 0.45 micron, to remove particulates) or an ion exchange resin membrane (for dissolved components). Above the filter or resin membrane surface, an x-ray transparent material, for example, kapton or beryllium, fitted with O-rings, confines the water sample within the filter cavity and provides the window through which x-ray analysis proceeds. In this way, frequent measurements (several per hour) are made of the incremental accumulation of metals while the filter or resin membrane remains in service.

7.4 The x-ray probe consists of both the excitation source to irradiate the sample and the detection device for returning fluorescence. The excitation source may be an electronic x-ray tube or a suitably chosen radioisotope. For efficient excitation, the excitation energy should be 1.5 to 2 times the fluorescent energy of the element(s) being monitored. For example, iron which fluoresces at 6.4 keV should be irradiated with a source in the range of 10 to 13 keV. Many x-ray tubes have variable power capability so voltage and amperage may be adjusted to optimize the analysis at hand. Alternatively, for iron analysis, an appropriate choice of radioisotope as an excitation source is curium-244 (Cm-244), which emits a line at approximately 12 keV.

7.5 For each measurement cycle, the following information is recorded in a continuously updated data file in the controlling personal computer (PC): date, time, mass measurement for each metal of interest, volume increment, and raw intensity data. The on-line control program, as well as several auxiliary programs, operate under the Microsoft Windows platform. The PC controls all aspects of monitor operation and stores all collected data. Monitoring results appear on the PC screen in real time during a monitoring session, as well as, being stored in continuously updated files in a subdirectory of the user's choice.

7.6 The data files' generated during an on-line session represent a record of cumulative metal mass as a function of cumulative sample volume during the course of the session. Since the units of these parameters are micrograms and liters respectively, the slope through the data at any point gives the metal concentration in ppb. A separate program, residing in the same Windows group as the on-line control program, automatically converts the raw data to ppb values as a function of time.

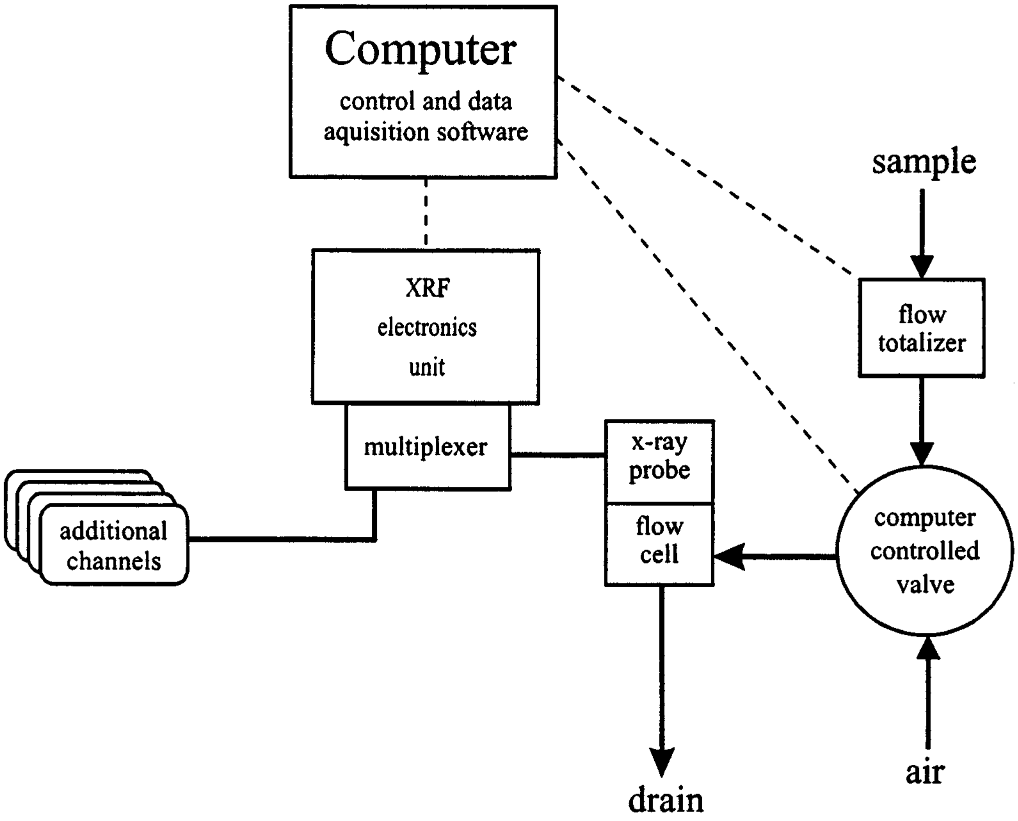

FIG. 1 Schematic of On-Line X-Ray Fluorescence Monitor

---

[3] Monitoring systems from DETORA Analytical, Inc., P.O. Box 2747, Alliance, OH 44601 were used in the preparation of this standard, and is the sole source of supply.

7.7 A schematic diagram of a typical configuration is shown in Fig. 1. This configuration shows only one channel or sampling system. Additional channels can be incorporated readily into the monitoring system.

7.8 Each channel comprises a separate flow cell, x-ray probe, flow totalizer, and valve switching system. Through the use of a multiplexer, several channels may share common electronics and software control. With a multi-channel system, several separate process streams may be monitored simultaneously. Another application of a multi-channel system is to separately monitor particulates (using a filter in one channel) and dissolved metals (using a resin membrane in another channel) in the same process stream.

7.9 There are no reagents involved in the operation of the monitor. Fresh filters are installed at the start of each monitoring session. The kapton window and O-rings may be replaced as needed.

8. Calibration

8.1 *Membrane Filter Standards*—Membrane filter standards for iron are prepared from an atomic absorption standard for iron (alternatively, a user may make up his or her own standard solution). The atomic absorption (AA) standard is 1000 ppm iron dissolved in dilute acid solution. Sodium hydroxide, or ammonia, solution is used to adjust measured aliquots of this standard to a pH of 10 to 11. Under these conditions, iron is insoluble and filterable. The resulting iron suspension is filtered through a 0.45 micron membrane filter and the filtrate analyzed by AA after appropriate acidification or digestion. Any iron determined in the filtrate is subtracted from the amount contained in the volume passed through the filter to determine the amount on the filter.

8.1.1 The aliquots of AA standard may be diluted with high purity water (ASTM Type 3 water is acceptable) prior to pH adjustment. The dilution provides more conveniently handled volumes, and the larger volumes will promote more uniform distribution of iron on the filter surface. The amount of dilution does not affect the total iron to be filtered.

8.1.2 This procedure is repeated to prepare filter standards covering a range of total iron from zero (blank filter) to three milligrams. The lowest prepared standard should be near the minimum detectable amount (see 12.2).

8.1.3 This procedure, without adjustment to high pH, may be used to prepare cation resin membrane standards covering, a range of total dissolved iron.

8.2 *Construction of Calibration Line*—Filter or resin membrane standards prepared as described in 8.1 are analyzed using the on-line x-ray probe to collect intensity data under the exact conditions of on-line service. This includes installing the filter or resin membrane in the flow chamber of the on-line system and analyzing through the kapton window.

8.2.1 The intensity data collected in this way is plotted against the known amounts of total iron and the equation for the best line through the data is determined by standard least squares regression techniques. For up to approximately 3 mg of total iron, the relationship is nearly linear. The resulting calibration equation is then used to convert intensity measurements of filters or resin membranes to iron mass during on-line operation.

8.2.2 The calibration curve parameters may be input to the x-ray control electronics unit or directly to the PC depending on the software configurations of the monitor. In either case, the intensity measurements during an on-line session are converted automatically to mass values and both are stored in the data file, which is updated continuously during operation.

8.2.3 This mass measurement (in micrograms) is used with the incremental volume total (litres) between measurements to give the desired concentration in micrograms per litre, or parts per billion (ppb).

9. Procedure

9.1 Install the apparatus according to the manufacturer's instructions. Establish delivery of a representative sample stream to the monitoring system in accordance with pertinent ASTM specifications and practices, respectively. (D 1192, D 1066, D 3370, D 4453, D 5540, and D 6301). Adjust sample flow, temperature and pressure to within the manufacturer's recommendations prior to delivering the sample stream to the instrument.

9.2 The instrument must be calibrated prior to use. To do this, the sample control valve must be in the air position, providing air flow through the entire system and allowing the sample line to drain. This is the default case when the instrument is first turned on or has been stopped after a sampling session. Close the manual air valve to stop air flow through the flow cell. Calibrate the apparatus according to the manufacturer's directions, following the guidelines given in Section 8.

9.3 Following calibration, install a new filter into the flow cell assembly following the manufacturer's directions. Both the sample control valve and the manual air valve should be closed. Through the entire filter installation procedure, the sample stream continues to drain.

9.4 After a new filter has been installed and the flow cell reassembled, open the manual air valve. This restores air flow to the system.

9.5 Begin the on-line control program. The first dialog panel displayed allows the user to enter test setup parameters or to start or stop testing. Prior to testing, the appropriate parameters must be identified by executing test setup as described in the manufacturer's directions. Various identifying information (plant name, process stream location, operator ID, etc.), as well as, operational parameters (sample accumulation time and x-ray scan duration) must be entered. Enter the appropriate information, following the manufacturer's recommendations and guidelines.

9.6 After test setup parameters have been entered and accepted, a monitoring session begins by the user activating the program. The system cycles between sample accumulation and x-ray analysis until the program is terminated by the user.

9.7 The need to change to a fresh filter or resin membrane is governed by different criteria. A filter may remain in service until one of two conditions arises: when the quantity of a element on a filter exceeds that of the highest standard used for calibration (see Section 9), or the build-up on the filter causes excessive flow restriction. Under conditions of low ppb metal concentrations, typical of nuclear power station feedwater, filters can remain in service for several days before one of these conditions arises. For anion or cation resin membranes, the useful life is governed by the ionic capacity of the resin. Additionally, ionic retention efficiency is dependent on the flow rate through the membrane. Both the capacity and the retention efficiency vary among manufacturers. Information on these parameters generally is available from the commercial suppliers.

10. Statistical Considerations

10.1 *Precision of the Instrumental Measurement*—The precision of the analytical instrumentation may be determined through repetitive measurements of the same sample without moving the sample between measurements. The standard deviation of such a series of measurements is a measure of the instrument precision. It is useful to use prepared calibration standards for this type of precision determination. Precision determinations should be made over a range of elemental concentrations, from the high to the low ends of the calibration range.

10.2 *Precision of the Measurement Technique*—The precision of the methodology involved in this test method may be determined through repetitive measurements of the same sample, removing and replacing the sample in the flow cell assembly between each measurement. The difference in the standard deviation of these results and that determined according to 10.1 is the additional variation contributed by operator technique.

10.3 Users should define acceptable precision requirements for a particular application.

11. Precision and Bias

11.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D 2777 since this test method is a continuous determination. This inability of Practice D 2777 procedures to obtain precision and bias data for continuous determinations is recognized and stated in its scope.

11.2 Refer to Section 10 for evaluation of instrumental and methodological precision.

12. Sensitivity

12.1 The detection limit of this monitor is defined somewhat differently than for traditional analytical instrumentation. By the nature of the concentrating effect of the filter or resin membrane, the detection limit of the monitor for an analyte is defined by accumulation time and flow rate, as well as, concentration. This is because, where a concentrating mechanism is involved, the detection limit refers to an amount, rather than a concentration, of a substance.

12.2 For an x-ray analyzer of the configuration and specifications used in the monitor, the detection limit for iron is approximately 3 µg distributed over the surface of a membrane filter with a diameter of 47 mm. The capability of the monitor for detection of low concentrations is a function of both the sample flow rate through the filter chamber and the sample accumulation time between measurements. Either or both of these may be increased, within practical limits, to improve the detection limit.

12.3 Typical operating values for these parameters during operation of the monitor in nuclear plants are sample flow rate of 400 ml/minute and a sample accumulation time of 20 minutes. Under these conditions, the detection limit for iron is 0.4 ppb.

13. Keywords

13.1 corrosion products; metals; on-line monitoring; water quality; x-ray fluorescence; XRF

BIBLIOGRAPHY

(**1**) Connolly, D.; Millet, P. "On-line Particulate Iron X-ray Monitor", ULTRAPURE WATER 11(1), pp. 61-65 (January/February 1994).
(**2**) Connolly, D.; Harvey, S. "On-line Corrosion Product Monitoring of Nuclear Plant Feedwater", ULTRAPURE WATER vol(no), pp. 28-31 (November 1995).
(**3**) Connolly, D.; Stauffer, C.; Millet, P. "On-line Monitoring of Particulate Iron Oxides in Steam Generator Feedwater Using X-ray Fluorescence", CORROSION 95 Paper No. 623.