Method Comparison Table

SM 5220 D	**14XXXCOD – April 1999**
1.0 Scope and Application In the presence of excess potassium dichromate and sulfuric acid, the oxygen equivalent of materials is measured by oxidation. The unreacted potassium dichromate is measured, and the result is defined as the mg of O_2 consumed in the reaction. This method is capable of measuring COD in the range of 20 – 900. The range could be extended to higher ranges by using smaller sample volumes or by diluting the sample. Additional sample manipulation could cause increased opportunity for error. The minimum level (ML) for this method is implied (20 mg/L) based on the test range cited. This method is applicable for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act.	**1.0 Scope and Application** In the presence of excess potassium dichromate and sulfuric acid, the oxygen equivalent of materials is measured by oxidation. This method is capable of measuring COD in the range of 4 – 10,000 mg/L. The concentration range of 4 – 500 mg/L consists of four different pre-measured Spectroquant® COD cell tests (Section 17.0, Table 1, items 14560, 14540, 14895, and 14690). These Spectroquant® COD cell tests measure the amount of potassium dichromate, which has not been reduced in the digestion. The absorbance measurement is performed at the wavelength maximum of potassium dichromate. The concentration range of 100 – 10,000 mg/L consists of three different pre-measured Spectroquant® COD cell tests (items 14541, 14691, and 14555). These Spectroquant® COD cell tests allow photometric measurement of the amount of the green trivalent chromium ion (which is formed in the oxidation process). The Spectroquant® COD cell test 500 – 10,000 mg/L (item 14555) utilizes a sample volume of one milliliter. The upper limit of this concentration range may be extended to higher levels by serial dilution of the test sample. The seven (7) different concentration range Spectroquant® COD cell tests help reduce the amount of sample manipulation, which could cause unnecessary occasion for error. The ML for this method is 4 mg/L, which is 5 times more sensitive than the ML for the standard reference method, SM 5220 D. This method is applicable for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act.
2.0 Summary of Method A small aliquot of homogenized, acidified sample is digested with digestion reagents. The digestion reagents (which can be prepared in the laboratory or purchased as commercially available products) include a known excess	**2.0 Summary of Method** A 1, 2, or 3 ml (dependent upon the Spectroquant® COD cell test, see Section 17.0, Table 1) aliquot of homogenized, acidified sample is measured into the appropriate Spectroquant® COD cell test. The pre-measured reagents

of potassium dichromate and sulfuric acid. Silver sulfate and mercuric sulfate are included in the reaction vessel as a catalyst and chloride complexing reagent, respectively. The reaction vessels are sealed and heated at 150°C for two hours. After heating, mixing and cooling the reaction vessels, the color intensity of the trivalent chromium, which has been formed from the reduction of the dichromate ion, and is measured photometrically at 600 nm.	contain a known excess of potassium dichromate and sulfuric acid. Silver sulfate and mercuric sulfate are included in the Spectroquant® COD cell tests as a catalyst and chloride complexing agent, respectively. The Spectroquant® COD cell tests are sealed and heated at 150°C for two hours. After heating, mixing, then cooling the Spectroquant® COD cell tests in the 4 – 500 mg/L concentration range, the amount of potassium dichromate (which has not been reduced in the reaction) is measured photometrically. The absorbance measurement is performed at the wavelength maximum of potassium dichromate (340nm and 445 nm). After heating, mixing, then cooling the Spectroquant® COD cell tests in the 100 – 10,000 mg/L concentration ranges, the color intensity of the trivalent chromium ion (which was formed from the reduction of the dichromate ion) is measured photometrically at 605 nm.
3.0 Definitions See section 18.0 – There are no terms, acronyms, or symbols which have been defined in this method.	**3.0 Definitions** See section 18.0 – This method defines, in great detail, the terms, acronyms, and symbols, which appear in the body of the method.
4.0 Interferences Volatile straight chain aliphatic compounds are not oxidized appreciably by this method. These compounds are oxidized more readily, however with the addition of silver sulfate to the reaction vessel. Halogens interfere to produce precipitants that are oxidized only partially. These interferences are largely overcome by complexing with mercuric sulfate. This test is not suitable for waters containing over 2,000 mg/L. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. Nitrite (NO_2^-) at elevated level, but as the NO_2^- levels in waters rarely exceed 1 or 2 mg/L, this is not considered a significant interference. If necessary, high NO_2^- levels, and interferences, can be overcome by the addition of sulfamic acid to the reflux vessel.	**4.0 Interferences** Volatile straight chain aliphatic compounds are not oxidized appreciably by this method. These compounds are oxidized more readily, however with the addition of silver sulfate to the Spectroquant® COD cell test. Halogens, notably chlorides, interfere to produce precipitants that are oxidized only partially. These interferences are largely overcome by complexing with mercuric sulfate. For waters containing over 2,000 mg/L of chloride, the sample can be diluted with distilled water to overcome the interferences associated with the chloride. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. Nitrite (NO_2^-) at elevated level, but as the NO_2^- levels in waters rarely exceed 1 or 2 mg/L, this is not considered a significant interference. If necessary, high NO_2^- levels, and interferences, can be overcome by the treatment of the test sample with sulfamic acid before digestion.
5.0 Safety	**5.0 Safety**

The reference method does not define any potential health risks associated with the use of the chemicals in this method, most notably, mercuric sulfate. The reference method does make reference to the necessity to mix the reagents and the sample thoroughly before heating. This will reduce the possibility of exposure to splattering from uneven heating, possible reagent leakage or explosion of vessel.	This method employs the use of COD test cells, containing pre-measured reagents, hence the handling of hazardous chemicals is significantly reduced. As with any analytical procedure, the analyst is cautioned to become familiar with the potential health hazards described in the reference Material Safety Data Sheet (MSDS) records. Each Spectroquant® COD cell test is also clearly labeled as to the contents, and any potential health hazards. This helps to insure the safety of the analysts involved. The use of the safety shield, which is provided with the thermoreactor, lessens the possibility of exposure to violent reactions resulting from product leakage during digestion.
6.0 Equipment and Supplies This method employs standard laboratory glassware for sampling (1L glass or plastic bottle). Standard glassware for sample handling include pipettes, blender, culture tubes (16 x 100-mm, 20 x 150-mm, and 25 x 150-mm). The digestion is accomplished using a block digester or oven. These devices may not be exact in their temperature settings. A spectrophotometer is used to measure the oxygen which has been consumed by the oxidizing reagent. The wavelength is set at 600 nm for the determination.	**6.0 Equipment and Supplies** This method employs all supplies, which are specified in method 5220 D. The photometric determination is accomplished using a filter photometer or with any other standard photometer. ***Spectroquant® Thermoreactor (block digester)*** The thermoreactor can be pre-set to designated reaction temperatures. It also has a built-in timer, which incorporates automatic shut-off. ***Spectroquant® COD Cell Test*** The reagents are pre-measured in 16 x 100 mm tubes (the Spectroquant® COD cell test). This approach eliminates the possibility of contamination due to residues remaining on laboratory washed glassware. ***Spectroquant® NOVA 60 Filter Photometer*** *COD cell identification* - The NOVA 60 is equipped with a Sample ID system. Each Spectroquant® cell test is bar coded, and when placed correctly in the cell compartment, the instrument recognizes the cell, and sets the instrument to the proper measuring parameters (i.e. item number, test range, cell format, wavelength and calibration data). Spectroquant® NOVA 60 can also store the sample information within its data files, for printing, downloading to alternate data storage location, or for easy retrieval. *Calibration* - The Spectroquant® NOVA 60 has been factory calibrated, and the readings obtained from the sample cells are automatically expressed as the COD concentration (mg O_2/L). The calibration curve can be

	verified, and the data from this verification can be stored, modified or re-entered at any time. The user cannot change the factory program setting. Instead, when the manufacturer generates new calibration data, they supply a new memo microchip (transponder) to the user for updating the system. ***<u>Other Photometric Devices</u>*** The use of other photometric equipment, which may be substituted for use with this method, is consistent with the reference method specifications.
7.0 Reagents and Standard This method incorporates the following chemicals which are prepared by the laboratory analyst: *Digestion solution* – potassium dichromate and mercuric sulfate dissolved in sulfuric acid. *Sulfuric acid reagent* – silver sulfate dissolved in conc. sulfuric acid. *Sulfamic acid* – ACS reagent grade *Potassium hydrogen phthalate (KHP) standard solution–* Potassium hydrogen phthalate dissolved in water.	**7.0 Reagents and Standards** This method combines, in proportions consistent with SM 5220 D, all of the reaction chemicals, which are specified in the reference method, into special optical quality glass 16 x 100-mm tubes (Spectroquant® COD cell test). The reagents include: excess potassium dichromate (specific to the Spectroquant® COD cell test concentration range), sulfuric acid, silver sulfate (catalyst), and mercuric sulfate (chloride complexing agent). The pre-measured reagents reduce the risk of error in preparation of the chemical reagents. Each Spectroquant® COD cell test is clearly labeled with the product number and hazard symbol to eliminate erroneous results. The KHP solutions have been incorporated into the quality control program, as initial precision and recovery (IPR), ongoing precision and recovery (OPR), and matrix spiking (MS) solutions. The use of these standard solutions increases the laboratory's potential to produce accurate data.
8.0 Sample Collection, Preservation, and Storage The sampling is performed in accordance with Standard Methods. The sample is collected in a glass or plastic bottle. The sample is preserved to a pH of less than 2. Because of the small sample volumes used for the procedure, the sample must be homogenized prior to delivery into the reaction cells. The samples should be stored at 4°C until analysis. The samples should be analyzed within 28 days.	**8.0 Sample Collection, Preservation, and Storage** The sampling is performed in accordance with Standard Methods. There are no differences in the way the samples are collected, preserved or stored in this method.
9.0 Quality Control There are no quality control guidelines incorporated into the body of this method.	**9.0 Quality Control** This method includes guidelines for initial demonstration of laboratory capability, quality control and quality assurance

	measurements. Initial demonstration of performance of the method is required. After initial performance has been established, the analyst is required to provide proof of continued performance through the analysis of ongoing precision and recovery standards. These are tested in conjunction with the entire analytical quality control batch (for up to 20 samples), which include: (1) laboratory blank, (1) laboratory control sample (OPR), (1) Spiked sample (MS), and (1) spiked sample duplicate (MSD).
10.0 Calibration and Standardization The spectrophotometer is calibrated using a blank and at least five (5) potassium hydrogen phthalate standards covering the concentration range of samples to be tested. The absorbances of the standards are plotted against the concentration. Absorbance readings from samples are plotted against this curve to obtain a concentration value. The calibration curve should be re-run if the linearity of the curve varies more than 5%, or with each new lot of reagents.	**10.0 Calibration and Standardization** Calibrate the analytical balance (for weighing potassium hydrogen phthalate) with class S certified weights. ***Spectroquant® NOVA 60 Filter Photometer*** The Spectroquant® NOVA 60 instrument is factory calibrated with standard reference material, and the products are shipped with Lot Certificates for calibration. ***Other Photometric Devices*** The calibration is performed as described in SM 5220 D (potassium hydrogen phthalate).
11.0 Procedure A small aliquot of sample is digested with the reagents listed above in a suitable reaction vessel, which is chosen based upon the size of reaction cell used. The cells are heated for two hours at 150°C to effect digestion. Once cooled, absorbance of the green trivalent chromium ion is determined at 600 nm. The results are plotted from the calibration curve (minimum of five points).	**11.0 Procedure** As in the reference method, a small volume of sample is introduced to the pre-measured digestion reagents (in a Spectroquant® COD cell test), and heated for two hours at 150°C to effect digestion. The reagent formulations are consistent with those cited in the reference method, yet are expanded to encompass a broad 4 – 10,000 mg/L concentration range, in contrast to the 20 – 900 mg/L range listed in the reference method. The 340 nm wavelength, a maximum absorbance range for chromate, offers the highest sensitivity and accuracy for the 4 – 40 mg/L concentration range (Section 17.0, Table 1 – Item 14560). In the 10 – 500 mg/L concentration range Spectroquant® COD cell tests, (Section 17.0, Table 1 - items 14540, 14895, and 14690) the absorbance measurement is performed at another maximum wavelength for chromate, 445 nm. In the 100 – 10,000 mg/L concentration range Spectroquant® COD cell tests (items 14541, 14691, and

	14555), the amount of the green trivalent chromium ion, which has been formed during the reaction, is measured at the wavelength of 605 nm.
12.0 Data Analysis and Calculations The reference method defines the calculation for dilution factor correction. The method does not address significant digits. The Minimum Level (ML) is implied from the concentration range 20 – 900 mg/L, as 20 mg/L.	**12.0 Data Analysis and Calculations** ***Spectroquant® NOVA 60 Photometer*** Results with the Spectroquant® NOVA 60 are displayed as COD concentration (mg O_2/L). ***Other Photometers*** Measurement of samples with equivalent photometric equipment allows for values to be plotted from calibration curves. This method defines the calculation for dilution factor correction in event that samples read outside the calibration range of the test. The Minimum Level (ML) for this method is 4 mg/L. If a result is obtained which is lower than this ML, report the result as less than the ML (<4 mg/L). Report results to two significant digits.
13.0 Method Performance Referenced in the method is precision and bias data obtained from forty-eight synthetic samples of standard potassium hydrogen phthalate solution, some with sodium chloride added as interference, and were tested in five laboratories.	**13.0 Method Performance** As in the SM 5220 D reference method, this method incorporates the same chemical components, in the same proportions, the same digestion time and temperature, and is determined similarly via photometric measurement. The precision and bias stated in the reference method are achievable by this method.
14.0 Pollution Prevention The reference method does not discuss pollution prevention.	**14.0 Pollution Prevention** The label on each Spectroquant® COD Cell Test informs the user of the contents and potential health risks. Furthermore, the Material Safety Data Sheets (MSDS) provide guidance for waste management. The packaging and use of pre-measured Spectroquant® COD Cell Tests is designed to minimize risks of spillage, and to reduce the amounts of the chemicals used. The laboratory is reminded to properly manage these reagents in the laboratory to reduce any threat to the environment. General practices, such as ordering of supplies, can seriously impact the amount of materials which require disposal in the laboratory. It is suggested that the laboratory only order supplies as demand dictates, to minimize expired materials requiring disposal.
15.0 Waste Management	**15.0 Waste Management**

The reference method does not discuss waste management.	Referenced in section 15.3 are two waste management documents for further information on this subject. In using this method, the laboratory must comply with all federal, state, and local regulations governing waste management.
16.0 References The reference method lists two journal publications in its bibliography. There are references regarding overcoming chloride interferences in the introduction section of this method.	**16.0 References** This proposed method includes in the reference section, existing method documents for COD, supplemental and related documents for safety and general laboratory practices. Also included is the instrument manual reference material, which outlines the calibration procedures for the Spectroquant® NOVA 60.
17.0 Tables, Diagrams, Flowcharts, and Validation Data The reference method includes a table of sample and reagent quantities for various vessels. This guide is useful in assisting analysts in preparing the digestion vessels properly (proportionally). There are no diagrams, flowcharts or validation data reports included in this method.	**17.0 Tables, Diagrams, Flowcharts, and Validation Data** Three tables are included in this method. ***Table 1*** This table summarizes the different Spectroquant® COD cell tests comprised in this method, concentration ranges for each Spectroquant® COD cell test, product numbers, sample volume required, chloride interference levels, and wavelength settings for photometric measurement. ***Table 2*** This table outlines the procedure for preparing calibration curve solutions for all seven Spectroquant® COD cell test concentration ranges for calibration of photometric devices (other than the Spectroquant® NOVA 60). ***Table 3*** This table outlines the standardized performance acceptance criteria for parameters cited from 40 CFR Part 136, Table IB. This data must be achieved when the analyst initiates the method, attempts to prove initial demonstration of performance, and also ongoing performance of the method.
18.0 Glossary The reference method does not have a glossary.	**18.0 Glossary** See Section 3.0 The glossary defines terminology used in the body of method. Much of the terms defined are specific to the quality control section of the method. These terms are not used, or defined, in the reference method.

	This section clearly defines the nomenclature of the products being proposed for use.