

# Method Comparison Table

**EPA 375.4**

**14XXSO4 – May 2000**

<p><b>1.0 Scope and Application</b>          For wastewater samples, in a weak hydrochloric acid solution, barium sulfate is precipitated with the addition of barium chloride.</p> <p>This method is intended for the analysis of sulfate on drinking and surface waters, domestic and industrial wastes. This method is capable of measuring sulfate in the range of 1 – 40 mg/L.</p> <p>The absorbance of the barium sulfate formed in the reaction, is measured at 420 nm on a photometric device.</p> <p>This method is applicable for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act.</p>	<p><b>1.0 Scope and Application</b>          For waters and wastewater samples, in a weak hydrochloric acid solution, barium sulfate is precipitated with the addition of barium chloride.</p> <p>This method is intended for the analysis of sulfate on drinking and surface waters, domestic and industrial wastes. This method is capable of measuring sulfate in the range of 5 – 1000 mg/L.</p> <p>The absorbance of the barium sulfate formed in the reaction, is measured at 525 nm for concentration range 5 to 250 mg SO<sub>4</sub><sup>2-</sup>/L<sup>-</sup> and at 820 nm for concentration range 100 –1000mg SO<sub>4</sub><sup>2-</sup>/L on a photometric device.</p> <p>Pure barium sulfate suspension has a linear spectrum. This method utilizes a wavelength of 525 nm for the range covering 5-250 mg/L, and 820 nm for range covering 100-1000 mg/L.</p> <p>There are two (2) concentration ranges included in this method. Use of pre-measured reagents, with increased concentration ranges (5 – 250 and 100-1,000 mg/L) reduces the amount of sample manipulation, which could cause the potential for technician error.</p> <p>This method is applicable for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act and Safe Drinking Water Act.</p>
<p><b>2.0 Summary of Method</b>          A 100-ml portion of sample (or an aliquot diluted to 100-ml) is placed into a 250-ml beaker or erlenmeyer flask. The sample is mixed with a magnetic stir plate. 5 ml of a conditioning reagent (containing hydrochloric acid, sodium chloride, an alcohol and glycerol) is added to the sample. An amount of barium chloride (0.2 – 0.3 ml capacity spoonful) is added to the sample.</p> <p>A one minute reaction time (while stirring) is begun. Immediately after one minute, the sample is poured into an absorbance cell. The absorbance (at 420 nm) is measured, by a photometric device, every 30 seconds for four minutes. The highest absorbance measurement is recorded.</p>	<p><b>2.0 Summary of Method</b>          Depending upon the Spectroquant® SO<sub>4</sub> cell test concentration range, a 1 or 5 ml aliquot (Section 17.0, Table 1) of homogenized sample is measured into a Spectroquant® SO<sub>4</sub> cell test. The pre-measured reagents contain a conditioning agent (containing hydrochloric acid, sodium chloride, an alcohol and glycerol). To this solution, one dose (70-75 mg) of barium chloride is added, and shaking vigorously mixes the cell.</p> <p>If present, sulfate will precipitate as barium sulfate. After at least a five-minute reaction period, the absorbance of the solution is measured at 525 nm. As the suspension includes fine barium sulfate particles, increased reaction time will result in settling, hence reduced absorbance of the precipitate. Swirl the cell gently prior to reading</p>

	absorbance past the five-minute reaction time.
<p><b>3.0 Definitions</b> This method does not define any specific terms used in the body of the method.</p>	<p><b>3.0 Definitions</b> See section 18.0</p>
<p><b>4.0 Interferences</b> Color and suspended matter interfere with the photometric measurement. To counter this potential positive interference, a sample blank, from which barium chloride has been omitted, is prepared.</p> <p>Silica in concentrations over 500 mg/L will interfere.</p> <p>Waters containing appreciable amounts of organic material may not satisfactorily precipitate barium sulfate.</p>	<p><b>4.0 Interferences</b> The advantage of measuring the absorbance at 525 nm is the reduction of interference caused by yellowish-brown colored wastewater samples at 525 nm. At 525 nm, the color of typical waste waters does not interfere to the degree that it affects measurement at 420 nm, therefore the measuring range is increased at 525 nm. At 420 nm, yellowish-brown colored wastewater samples yield a high absorbance. At 420 nm, it is necessary to incorporate an untreated sample as a blank, to counter this potential positive interference. Utilizing a blank in this way decreases the potential range of measurement of the sample.</p> <p>Suspended matter and turbidity do affect the measurement at either wavelength (525 nm or 420 nm), therefore, it may be necessary to pre-filter samples prior to analysis. As all inorganic sulfates (with the exception of barium and strontium sulfate) are water soluble, filtration will not affect the recovery of sulfates in the sample. Filtration may not remove all turbidity; therefore an untreated blank sample may be necessary.</p> <p>Elevated levels of barium sulfate precipitate affect the linearity of the spectrum, and this interference is much less apparent at 820 nm and to a lesser degree at 525 nm. The use of the wavelength 820 nm, allows for the measurement of much higher concentrations of sulfate, without compromising the linearity of the spectrum (100 – 1000 mg SO<sub>4</sub><sup>2-</sup>/L).</p> <p>Waters containing appreciable amounts of organic material may not satisfactorily precipitate barium sulfate.</p> <p><b>Method 14548:</b> Silver ion interferes in concentration &gt; 2 mg/L, Sulfide in concentration higher than 10 mg/L, dichromate and sulfite in concentration higher than 50 mg/L, Thiosulfate in concentration higher tahn 25 mg/L. EDTA interferes and must be absent.</p> <p><b>Method 14564:</b> EDTA must be absent. Silver ion interferes if more than 10 mg/L are present, Sulfide greater than 50 mg/L and thiosulfate greater than 100 mg/L.</p>

<p><b>5.0 Safety</b> There is no section describing the safety risks associated with the performance of this method.</p>	<p><b>5.0 Safety</b> Some of the chemicals and materials used in this test procedure pose a health risk, if not handled properly. Use appropriate eye protection and clothing when performing this method. If contact with skin occurs, flush immediately with water, and refer to the material safety data sheets. Follow instructions carefully.</p> <p>The use of pre-measured reagents greatly reduces the risk that the analyst will come in contact with chemicals used in this test kit.</p>
<p><b>6.0 Equipment and Supplies</b> This method employs standard laboratory glassware for sampling (1L glass or plastic bottle). Standard glassware for sample handling including pipettes, beaker, magnetic stir plate, and culture tubes (16 x 100 mm).</p> <p>A spectrophotometer is used to measure the absorbance of the barium sulfate precipitated by the addition of barium chloride in a weakly acidic solution. The wavelength is set at 420 nm for the determination.</p>	<p><b>6.0 Equipment and Supplies</b> This method relies on manual mixing of reagents, rather than mixing with a magnetic stir plate. All other materials are consistent with the reference method.</p> <p>The reagents are prepackaged in the culture tubes; therefore the possibility of laboratory contamination is eliminated.</p> <p><b><u>Spectroquant® NOVA 60 Filter Photometer</u></b> <i>Sulfate cell identification</i> - The Spectroquant® 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 wavelength. 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.</p> <p><i>Calibration</i> - The Spectroquant® NOVA 60 has been factory calibrated, and the readings obtained from the sample cells are automatically expressed as the sulfate concentration (mg/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 can not change the factory program settings. When appropriate the manufacturer supplies a new memo chip (transponder) containing new calibration data.</p> <p><b><u>Other Photometric Devices</u></b> The use of other photometric equipment, which may be substituted for use with this method, is consistent with the reference method specifications.</p>

<p><b>7.0 Reagents and Standard</b>  This method incorporates the following chemicals which are prepared by the laboratory analyst:</p> <p><i>Conditioning reagent</i> – hydrochloric acid, water, alcohol, sodium chloride and glycerol.</p> <p><i>Barium Chloride</i> – ACS grade reagent.</p> <p><i>Sulfate Standard solution</i>-for preparation of the standard calibration curve.</p>	<p><b>7.0 Reagents and Standards</b>  This method combines all chemicals (except the barium chloride) which are specified in the reference method, into a 16 x 100-mm culture tube. The pre-measured reagents reduce the risk of error from technician error in preparation of the chemical reagents.</p> <p>The ratio of the chemicals in the reagent cells is consistent with the theory of the reference method. The sample is mixed with the conditioning reagent, in the test cell, and then barium chloride is introduced using a measuring spoon (1 dose = 70-75 mg).</p> <p>A 1,000 mg/L sulfate standard solution (Item # 19813, Section 7.4) is also provided for in the test procedure. This commercially available stock solution is standardized using the same procedure stated in 5.4.1.1 of the reference method.</p>
<p><b>8.0 Sample Collection, Preservation, and Storage</b>  The sampling is performed in accordance with Standard Methods. The sample is collected in a glass or plastic bottle. The sample is preserved refrigerated until analysis. The samples should be analyzed within 7 days.</p>	<p><b>8.0 Sample Collection, Preservation, and Storage</b>  For this method, the samples are collected in the same way as referenced in EPA 375.4. There are no differences.</p>
<p><b>9.0 Quality Control</b>  There are no quality control guidelines written into this method.</p>	<p><b>9.0 Quality Control</b>  This method includes guidelines for initial demonstration of laboratory capability, quality control and quality assurance measurements.</p> <p>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).</p>

<p><b>10.0 Calibration and Standardization</b>  The standard sulfate reagent for calibration curve, is standardized with Sodium carbonate solution for accuracy. The method calls for a calibration curve consisting of eight standard solutions (at 5 mg/L intervals) spanning the 5-40 mg/L concentration range.</p>	<p><b>10.0 Calibration and Standardization</b>  <u><b>Spectroquant® NOVA 60 Filter Photometer</b></u>  The Spectroquant® NOVA 60 instrument is factory calibrated with standard reference material, and the products are shipped with Lot Certificates for calibration.</p> <p><u><b>Other Photometric Devices</b></u>  The calibration is performed as described in EPA 375.4 (standard sulfate solution –1,000 mg/L – item No.19813 or equivalent).</p>
<p><b>11.0 Procedure</b>  A 100-ml aliquot of sample mixed with the conditioning reagent for a short period. A spoonful (0.2 – 0.3 ml) of barium chloride is added, while still mixing. After exactly one minute of stirring, the sample is poured into an absorbance cell. Absorbance readings (at 420 nm) are taken every 30 seconds. The highest absorbance reading obtained in the four-minute period is recorded. This absorbance measurement is plotted against a calibration curve to obtain concentration in the sample.</p>	<p><b>11.0 Procedure</b>  Adjust pH of sample and filter (if necessary). A small volume of sample is introduced to the pre-measured Spectroquant® SO<sub>4</sub> cell test, which contains the conditioning reagents. The sample and reagents are mixed well.</p> <p>Immediately, one dose (70-75 mg) of barium chloride is added to the test cell. Again, the Spectroquant® SO<sub>4</sub> cell test is mixed vigorously to effect complete dissolution of the barium chloride.</p> <p>After exactly 5 minutes, measure the sulfate on the NOVA 60 depending on the concentration range at 525 nm (for concentration range 5-250 mg/L) or 820 (for concentration range 100-1000 mg/L). Do not wait longer than five minutes to obtain the concentration of the sulfate in the sample cell, as the finer particles begin to settle out of the solution.</p> <p>The reagent formulations are consistent with those cited in the reference method. The range is expanded through the use of the wavelengths 525 nm and 820 nm, which (in some cases) offer an alternative to sample blanking (to overcome color interferences).</p>

<p><b>12.0 Data Analysis and Calculations</b>  The reference method defines the standardization of the sulfate standard material for curve preparation.</p> <p>The method lists the minimum level (ML) as 1 mg/L, and the concentration range is 1 – 40 mg/L.</p>	<p><b>12.0 Data Analysis and Calculations</b>  <u><i>Spectroquant® NOVA 60 Photometer</i></u>  Results with the Spectroquant® NOVA 60 are displayed as sulfate concentration (mg/L). The range of the test is 5 – 1,000 mg/L.</p> <p><u><i>Other Photometers</i></u>  Measurement of samples with equivalent photometric equipment allows for values to be plotted from calibration curves.</p> <p>This method defines the calculation for dilution factor correction in event that samples read outside the calibration range of the test.</p> <p>The Minimum Level (ML) for method 14548 is 5 mg/L for method 14564 100 mg/L. If a result is obtained which is lower than this ML, report the result as less than the ML (&lt;5 mg/L for method 14548 and 100 mg/L for method 14564 respectively). Report results to two significant digits.</p>
<p><b>13.0 Method Performance</b>  There is a table of validation data, obtained from a FWPCA Method study, for mineral and physical analyses. Section 8.0 of EPA 375.4 lists precision and accuracy data obtained from 34 analysts in 16 laboratories on six synthetic water samples are no diagrams, flowcharts or validation data reports included in this method.</p>	<p><b>13.0 Method Performance</b>  As in the EPA 375.4 reference method, this method incorporates the same chemical components, in the same proportions, the same reaction times, and is determined similarly via photometric measurement. This method’s performance is enhanced by the use of the wavelength 525 nm to overcome interference from color, and the use of wavelength 820 nm provides better linearity for this concentration range for measurement of wastewater samples.</p> <p>The precision and bias stated in the reference method are achievable by this method.</p>

<p><b>14.0 Pollution Prevention</b> The reference method does not discuss pollution prevention.</p>	<p><b>14.0 Pollution Prevention</b> The label on each Spectroquant® cell test informs the user of the contents and any potential health risks. Furthermore, the Material Safety Data Sheets (MSDS) provide guidance for waste management. The packaging and use of pre-measured Spectroquant® SO<sub>4</sub> cell tests is designed to minimize risks of spillage, and to reduce the amounts of the chemicals used.</p> <p>The laboratory is reminded to properly manage these reagents in the laboratory to reduce any threat to the environment.</p> <p>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.</p>
<p><b>15.0 Waste Management</b> The reference method does not discuss waste management.</p>	<p><b>15.0 Waste Management</b> Referenced in section 15.3 are two waste management documents for further information on this subject.</p> <p>In using this method, the laboratory must comply with all federal, state, and local regulations governing waste management.</p>
<p><b>16.0 References</b> The reference method lists two method references its bibliography. There is also a reference to a method study performed to achieve the precision and accuracy data (in Section 8.0).</p>	<p><b>16.0 References</b> This proposed method includes in the reference section, existing method documents for sulfate, 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.</p>

**17.0 Tables, Diagrams, Flowcharts, and Validation Data**

There is a table of validation data, obtained from a FWPCA Method study, for mineral and physical analyses. Section 8.0 of EPA 375.4 lists precision and accuracy data obtained from 34 analysts in 16 laboratories on six synthetic water samples 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® SO<sub>4</sub> cell tests comprised in this method, concentration ranges for each Spectroquant® SO<sub>4</sub> cell test, product numbers, sample volume required, wavelength settings for photometric measurement, and method codes.

**Table 2**

This table outlines the procedure for preparing calibration curve solutions for both Spectroquant® SO<sub>4</sub> cell test concentration ranges for calibration of photometric devices (other than the Spectroquant® NOVA 60).

**Table 3**

This table outlines the performance acceptance criteria, 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.