

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 60, 61, and 63

[FRL-5880-8]

RIN 2060-AG21

Amendments for Testing and Monitoring Provisions

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule: Amendments.

SUMMARY: This action proposes amendments to 40 CFR parts 60, 61, and 63 to reflect miscellaneous editorial changes and technical corrections throughout the parts in sections pertaining to source testing or monitoring of emissions and operations, and proposes to add Performance Specification 15 (PS 15) to Appendix B of Part 60. In addition, the test methods in Appendix A of Part 60, Appendix B of Part 61, Appendix A of Part 63, and the performance specifications in Appendix B of Part 60 are proposed to be restructured in the format recommended by the Environmental Monitoring Management Council (EMMC) to achieve uniformity and consistency between Agency methods. The editorial changes and technical corrections to the subparts, test methods, and/or performance specifications in Parts 60, 61, and 63 are proposed to maintain the intent of the regulations.

DATES: *Comments.* Comments must be received on or before October 27, 1997 unless a hearing is requested by September 8, 1997. If a hearing is requested, written comments must be received by October 14, 1997.

Public Hearing. Anyone requesting a public hearing must contact EPA no later than September 8, 1997. If a hearing is held, it will take place on September 10, 1997, beginning at 9:00 a.m.

Request To Speak at Hearing. Persons wishing to present oral testimony must contact EPA by September 10, 1997.

ADDRESSES: *Comments.* Comments should be submitted (in duplicate, if possible) to: Air and Radiation Docket and Information Center (6102), Attention Docket No. A-97-12 (see

docket section below), room M-1500, U.S. Environmental Protection Agency, 401 M Street, SW., Washington, DC 20460. The Agency requests that a separate copy also be sent to the person listed in the **FOR FURTHER INFORMATION CONTACT** section below.

Public Hearing. If anyone contacts EPA requesting a public hearing, it will be held at the EPA's Emissions Measurement Laboratory, Research Triangle Park, North Carolina. Persons interested in attending the hearing or wishing to present oral testimony should notify Ms. Lala Cheek (MD-19), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, telephone (919) 541-5545.

Docket. Docket No. A-97-12, containing materials relevant to this rulemaking, is available for public inspection and copying between 8:00 a.m. and 5:30 p.m., Monday through Friday, except for Federal holidays, at the EPA's Air and Radiation Docket and Information Center, Room M-1500, U.S. Environmental Protection Agency, 401 M Street, SW., Washington, DC 20460; telephone (202) 260-7548. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Mr. Foston Curtis, Emission Measurement Center (MD-19), Emissions, Monitoring, and Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-1063 or at fax number (919) 541-1039.

SUPPLEMENTARY INFORMATION: The information presented in this preamble is organized as follows:

- I. Background and Purpose
- II. EMMC Format
- III. Significant Technical Revisions to Specific Test Methods, Performance Specifications, and Rules
 - A. General
 - B. ASTM Methods Updates
 - C. Continuous Instrumental Methods (Part 60, Appendix A)—Methods 3A, 6C, 7F, 10, and 20
 - D. Method 5 (Part 60, Appendix A)
 - E. Method 5E (Part 60, Appendix A)
 - F. Method 511 (Part 60, Appendix A)
 - G. Method 18 (Part 60, Appendix A)
 - H. Methods 306, 306A, and 306B (Part 63, Appendix A)
- IV. Addition of Performance Specification 15
- V. Copies of Regulatory Text
- VI. Administrative Requirements

- A. Docket
- B. Office of Management and Budget Review
- C. Regulatory Flexibility Act
- D. Paperwork Reduction Act
- E. Unfunded Mandates Reform Act

I. Background and Purpose

As part of its efforts to promote methods consolidation and integration between EPA Program Offices, the EMMC developed a consensus format for documentation of analytical methods. The Office of Air and Radiation has adapted the format for its new methods and is attempting to update its existing methods to this format. The EMMC format is shown in Section II. To achieve consistency between the test methods and performance specifications, EPA is proposing to restructure the test methods and performance specifications shown in Table 1 in the EMMC format. In addition, EPA reviewed the test methods and performance specifications and associated regulations in 40 CFR Parts 60, 61, and 63 and found that corrections and revisions were necessary. The corrections and revisions consisted primarily of typographical errors, technical errors in equations and diagrams, and narrative that is no longer applicable due to more recent additions. However, a few methods required further revision due to needed technical updates and comments received from the public. These methods are discussed in Section III. It is important to note that although numerous technical corrections were made to portions of the subparts in Parts 60, 61, and 63, changes were not made to any compliance standard, reporting, or recordkeeping requirement. For this notice, EPA is only proposing revisions to sections of the subpart pertaining to source testing or monitoring of emissions and operations.

II. EMMC Format

The test methods and performance specifications listed in Table 1 are being proposed in the restructured format shown in Table 2 which is recommended by EMMC. Only in a few instances were there any deviations from this recommended format.

TABLE 1.—TEST METHODS AND PERFORMANCE SPECIFICATIONS RESTRUCTURED IN THE EMMC FORMAT

40 CFR part 60, appendix A	40 CFR part 60, appendix B	40 CFR 61, appendix B	40 CFR 63, appendix A
1, 1a	PS-2	101, 101a	303, 303a
2, 2a, 2b, 2c,	PS-3	102	304a,
2d, 2e	PS-4, PS-4a	103	304b
3, 3a, 3b	PS-5	104	305

TABLE 1.—TEST METHODS AND PERFORMANCE SPECIFICATIONS RESTRUCTURED IN THE EMMC FORMAT—Continued

40 CFR part 60, appendix A	40 CFR part 60, appendix B	40 CFR 61, appendix B	40 CFR 63, appendix A
4	PS-6	105	306,
5, 5a, 5b, 5d,	PS-7	106	306a,
5e, 5f, 5g, 5h	PS-8	107, 107a	306b
6, 6a, 6b, 6c	PS-9	108	
7, 7a, 7b, 7c,		108a	
7d, 7e		108b	
8		108c	
10, 10a, 10b		111	
11			
12			
13a, 13b			
14			
15, 15a			
16, 16a, 16b			
17			
18			
19			
20			
21			
22			
23			
24, 24a			
25, 25a, 25b,			
25c, 25d, 25e			
26, 26a			
27			
28, 28a			
29			

TABLE 2.—EMMC FORMAT

Section No.	Section heading
1.0	Scope and Application.
2.0	Summary of the Method.
3.0	Definitions.
4.0	Interferences.
5.0	Safety.
6.0	Equipment and Supplies.
7.0	Reagents and Standards.
8.0	Sample Collection, Preservation, Storage and Transport.
9.0	Quality Control.
10.0	Calibration and Standardization.
11.0	Analytical Procedure.
12.0	Calculations and Data Analysis.
13.0	Method Performance.
14.0	Pollution Prevention.
15.0	Waste Management.
16.0	References.
17.0	Tables, Diagrams, Flowcharts, and Validation Data.

III. Significant Technical Revisions to Specific Test Methods, Performance Specifications, and Rules

A. General

A safety section (Section 5) was added to most of the test methods and performance specifications. This section discusses only those safety issues specific to the method and any target analytes or reagents that pose specific toxicity or safety issues.

B. ASTM Methods Updates

The American Society for Testing and Materials assisted EPA in revising test method references of ASTM methods by providing an update of all ASTM procedures cited in the test methods. Many Agency methods cite obsolete versions of ASTM methods that have been improved and redated or redesignated since the EPA methods were promulgated. Where appropriate, the redated and redesignated versions are included to add flexibility and clarify which methods may be used. In addition, the Incorporation by Reference citations in § 60.17 are amended to add the updated ASTM versions. The Agency is grateful for ASTM's assistance in this effort.

C. Continuous Instrumental Methods (Part 60, Appendix A)—Methods 3A, 6C, 7E, 10, and 20

The continuous instrumental methods have been coordinated to require the same performance specifications and, where applicable, the same testing procedures and equipment specifications.

D. Method 5 (Part 60, Appendix A)

Section 6.1.1.7 (formerly Section 2.1.6) specifies that a temperature sensor be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas and that the temperature around the filter holder be

regulated and monitored during sampling. EPA recognized that, depending on the sampling apparatus, temperature in the heating area may be measured at different locations (e.g., near the heater or at the top of the heated area) resulting in deviations from the recommended temperature range of 248±25°F. This modification was made so that temperature inside the heating area is measured at a consistent location in the gas stream. This modification requires that an extra temperature sensor be used with the filter heating system.

E. Method 5E (Part 60, Appendix A)

Section 6.3.4 (formerly Section 2.3.4) no longer specifies the Beckman Model 915 analyzer with a 215 B infrared or equivalent. Since the Beckman Model 915 is no longer manufactured, the EPA determined that the Rosemount Model 2100A TOC analyzer was comparable to the Beckman 915 model. As a result, Section 6.3.4 no longer specifies the Beckman Model 915 with 215 B infrared or equivalent but instead, the Rosemount Model 2100A TOC analyzer.

F. Method 5H (Part 60, Appendix A)

Section 7.3.4.1 (formerly Section 3.3.1.4) has been revised to specify that only three calibration gas levels (high-range, mid-range, and zero gases) are needed to calibrate the carbon dioxide, carbon monoxide, and sulfur dioxide

(SO₂) analyzers instead of four calibration gas levels. The low-range calibration gas is no longer required. This revision is consistent with the gas levels used to calibrate the SO₂ analyzer as described in Section 7.4 (formerly Section 5.3) of Method 6C (Determination of Sulfur Dioxide Emissions from Stationary Sources).

G. Method 18 (Part 60, Appendix A)

The Agency is soliciting comments on procedural modifications to Method 18 being proposed in this action. In the direct interface sampling procedure, the requirement for two consecutive samples to have less than 5 percent difference is being replaced with taking 5 consecutive samples per run. This modification allows for direct interface sampling to be used in cases where the process is highly variable. The adsorbent tube procedure is being modified to allow the source to choose any commercially available adsorbent material, instead of relying on the few adsorbents listed in the previous version of the method. In preparing calibration gases, it is proposed to allow the use of gas dilution instruments meeting the requirements of Method 205 of 40 CFR part 51, appendix M.

H. Methods 306, 306A, and 306B (Part 63, Appendix A)

Numerous editorial revisions were made to clarify the requirements of Methods 306, 306A, and 306B. The applicability sections of Methods 306, 306A, and 306B have been revised to add continuous chromium plating at iron and steel facilities to the list of source categories to which these methods apply. The requirement for filtration of all samples to be analyzed by ion chromatography has been eliminated from Section 9.2 (formerly Section 5.2.3) of Method 306 and Section 9.2 (formerly Section 5.2.3) of Method 306A. Instead, a qualifying note has been added stating that filtration is not required if a sample does not contain particulate matter. The filtration procedure would only apply when visible particulate is present in the sample (chromium electroplating and anodizing baths emit little, if any particulate); when needed, the tester is referred to the filtration procedure in Method 0061 in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Manual*, November 1986. Section 9.2.2 (formerly Section 5.1) of Method 306 has been revised to modify the post-sampling pH requirement for the sodium bicarbonate absorbing solution when it will be submitted to analysis by ion chromatography for hexavalent

chromium. The pH must be ≥ 8.0 rather than ≥ 8.5 , as the sodium bicarbonate solution does not reach a pH of 8.5. This requirement has also been added to Section 9.2.2 of Method 306A. Specific requirements for sample storage and sample holding times have been added to Sections 9.3 and 9.4, respectively, of Methods 306 and 306A. Section 9.1.2.3 (formerly Section 5.1.2.3) of Method 306A has been revised to add an option to adjust the sample volume for leaks discovered during the post-test leak-check. This option is consistent with that of Method 5 (40 CFR part 60, appendix A).

IV. Addition of Performance Specification 15

Performance Specification 15 is being proposed for addition to Appendix B of Part 60. Performance specification 15 may be used by sources to certify extractive Fourier Transform Infrared spectroscopy (FTIR) continuous emission monitors for regulated pollutants. The specification will determine the acceptability of FTIR continuous emission monitoring systems and is not source-specific. The procedure gives the source the option of using several techniques for FTIR certification including relative accuracy testing, spiking of target compounds, and comparison of dual instruments.

V. Copies of Regulatory Text

The text of the other proposed amendments is not included in this **Federal Register** action because of the magnitude of the reformatted test methods and amendments. The significant proposed amendments are discussed fully in this preamble. Performance Specification 15, which is a new procedure, is being published with this action as a proposed amendment to appendix B to part 60. The unpublished proposed amendments are available in Docket A-97-12 or by request from the Air and Radiation Docket and Information Center (see **ADDRESSES**) or the EPA contact person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section. The proposed amendments may also be obtained over the Internet at <http://www.epa.gov/oar/oaqps/emc>; choose the "Test Methods" menu, then choose "Proposed Test Methods." The amendments will be listed on the EPA Technology Transfer Network (TTN). The TTN is a network of electronic bulletin boards developed and operated by the Office of Air Quality Planning and Standards. The TTN provides information and technology exchange in various areas of air pollution control. The service is free, except for the cost

of the phone call. Dial (919) 541-5742 for data transfer of up to a 14,400 bps modem. Select TTN Bulletin Board: "Emission Measurement Technical Information Center (EMTIC)" and select menu item "Proposed Methods." If more information on the operation of the TTN is needed, contact the systems operator at (919) 541-5384.

VI. Administrative Requirements

A. Docket

The docket is an organized and complete file of all information submitted to or otherwise considered by EPA in the development of this proposed rulemaking. The principal purposes of the docket are: (1) To allow interested parties to identify and locate documents so that they can effectively participate in the rulemaking process, and (2) to serve as the record in case of judicial review (except for interagency review materials) [Clean Air Act Section 307(d)(7)(A)].

B. Office of Management and Budget Review

Under Executive Order 12866 (58 FR 51735 October 4, 1993), EPA is required to judge whether a regulation is "significant" and therefore subject to Office of Management and Budget (OMB) review and the requirements of this Executive Order to prepare a regulatory impact analysis (RIA). The Order defines "significant regulatory action" as one that is likely to result in a rule that may:

- (1) Have an annual effect on the economy of \$100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or communities;
- (2) Create a serious inconsistency or otherwise interfere with an action taken or planned by another agency;
- (3) Materially alter the budgetary impact of entitlements, grants, user fees, or loan programs, or the rights and obligation of recipients thereof; or
- (4) Raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order. This rulemaking does not impose emission measurement requirements beyond those specified in the current regulations, nor does it change any emission standard. The Agency has determined that this regulation would result in none of the adverse economic effects set forth in Section 1 of the Order as grounds for finding the regulation to be a significant rule. The Agency has,

therefore, concluded that this regulation is not a significant rule under Executive Order 12866.

C. Regulatory Flexibility Act

The EPA has determined that it is not necessary to prepare a regulatory flexibility analysis in connection with this proposed rule. The EPA has also determined that this rule will not have a significant adverse impact on a substantial number of small businesses. This rulemaking does not impose emission measurement requirements beyond those specified in the current regulations, nor does it change any emission standard. As such, it will not present a significant economic impact on a substantial number of small businesses.

D. Paperwork Reduction Act

The rule does not impose or change any information collection requirements subject to OMB review under the Paperwork Reduction Act, 44 U.S.C. 3501 *et seq.*

E. Unfunded Mandates Reform Act

Under Section 202 of the Unfunded Mandates Reform Act of 1995 ("Unfunded Mandates Act") signed into law on March 22, 1995, EPA must prepare a budgetary impact statement to accompany any proposed or final rule that includes a Federal mandate that may result in estimated costs to State, local, or tribal governments in the aggregate, or to the private sector, of \$100 million or more. Under Section 205, EPA must select the most cost-effective and least burdensome alternative that achieves the objectives of the rule and is consistent with statutory requirements. Section 203 requires EPA to establish a plan for informing and advising any small governments that may be significantly or uniquely impacted by the rule.

The EPA has determined that the action proposed today does not include a Federal mandate that may result in estimated costs of \$100 million or more to either State, local, or tribal governments in the aggregate, or to the private sector, nor does this action significantly or uniquely impact small governments, because this action contains no requirements that apply to such governments or impose obligations upon them. Therefore, the requirements of the Unfunded Mandates Act do not apply to this action.

List of Subjects in 40 CFR Part 60

Environmental protection, Air pollution control, New sources, Test methods and procedures, Performance

specifications, Continuous emission monitors.

40 CFR Part 61

Environmental protection, Air pollution control, Test methods and procedures.

40 CFR Part 63

Environmental protection, Air pollution control, Hazardous air pollutants, Test methods and procedures.

Dated: August 18, 1997.

Carol M. Browner,
Administrator.

It is proposed that 40 CFR part 60 be amended as follows:

1. The authority citation for part 60 continues to read as follows:

Authority: 42 U.S.C. 7401, 7411, 7414, 7416, 7601 and 7602.

2. By adding Performance Specification 15 in numerical order to Appendix B to read as follows:

Appendix B—Performance Specifications

* * * * *

Performance Specification 15— Performance Specification for Extractive FTIR Continuous Emissions Monitor Systems in Stationary Sources

1.0 *Scope and Application.* 1.1 *Analytes.* This performance specification is applicable for measuring all hazardous air pollutants (HAPs) which absorb in the infrared region and can be quantified using Fourier Transform Infrared Spectroscopy (FTIR), as long as the performance criteria of this performance specification are met. This specification is to be used for evaluating FTIR continuous emission monitoring systems for measuring HAPs regulated under Title III of the 1990 Clean Air Act Amendments. This specification also applies to the use of FTIR CEMs for measuring other volatile organic or inorganic species.

1.2 *Applicability.* A source which can demonstrate that the extractive FTIR system meets the criteria of this performance specification for each regulated pollutant may use the FTIR system to continuously monitor for the regulated pollutants.

2.0 *Summary of Performance Specification.* For compound-specific sampling requirements refer to FTIR sampling methods (e.g., reference 1). For data reduction procedures and requirements refer to the EPA FTIR Protocol (reference 2), hereafter referred to as the "FTIR Protocol." This specification describes sampling and analytical procedures for quality assurance. The infrared spectrum of any absorbing compound provides a distinct signature. The infrared spectrum of a mixture contains the superimposed spectra of each mixture component. Thus, an FTIR CEM provides the capability to continuously measure multiple

components in a sample using a single analyzer. The number of compounds that can be speciated in a single spectrum depends, in practice, on the specific compounds present and the test conditions.

3.0 *Definitions.* For a list of definitions related to FTIR spectroscopy refer to Appendix A of the FTIR Protocol. Unless otherwise specified, spectroscopic terms, symbols and equations in this performance specification are taken from the FTIR Protocol or from documents cited in the Protocol. Additional definitions are given below.

3.1 FTIR Continuous Emission Monitoring System (FTIR CEM).

3.1.1 *FTIR System.* Instrument to measure spectra in the mid-infrared spectral region (500 to 4000 cm^{-1}). It contains an infrared source, interferometer, sample gas containment cell, infrared detector, and computer. The interferometer consists of a beam splitter that divides the beam into two paths, one path a fixed distance and the other a variable distance. The computer is equipped with software to run the interferometer and store the raw digitized signal from the detector (interferogram). The software performs the mathematical conversion (the Fourier transform) of the interferogram into a spectrum showing the frequency dependent sample absorbance. All spectral data can be stored on computer media.

3.1.2 *Gas Cell.* A gas containment cell that can be evacuated. It contains the sample as the infrared beam passes from the interferometer, through the sample, and to the detector. The gas cell may have multi-pass mirrors depending on the required detection limit(s) for the application.

3.1.3 *Sampling System.* Equipment used to extract sample from the test location and transport the gas to the FTIR analyzer. Sampling system components include probe, heated line, heated non-reactive pump, gas distribution manifold and valves, flow measurement devices and any sample conditioning systems.

3.2 *Reference CEM.* An FTIR CEM, with sampling system, that can be used for comparison measurements.

3.3 *Infrared Band (also Absorbance Band or Band).* Collection of lines arising from rotational transitions superimposed on a vibrational transition. An infrared absorbance band is analyzed to determine the analyte concentration.

3.4 *Sample Analysis.* Interpreting infrared band shapes, frequencies, and intensities to obtain sample component concentrations. This is usually performed by a software routine using a classical least squares (cls), partial least squares (pls), or K- or P-matrix method.

3.5 *(Target) Analyte.* A compound whose measurement is required, usually to some established limit of detection and analytical uncertainty.

3.6 *Interferant.* A compound in the sample matrix whose infrared spectrum overlaps at least part of an analyte spectrum complicating the analyte measurement. The interferant may not prevent the analyte measurement, but could increase the analytical uncertainty in the measured

concentration. Reference spectra of interferants are used to distinguish the interferant bands from the analyte bands. An interferant for one analyte may not be an interferant for other analytes.

3.7 Reference Spectrum. Infrared spectra of an analyte, or interferant, prepared under controlled, documented, and reproducible laboratory conditions (see Section 4.6 of the FTIR Protocol). A suitable library of reference spectra can be used to measure target analytes in gas samples.

3.8 Calibration Spectrum. Infrared spectrum of a compound suitable for characterizing the FTIR instrument configuration (Section 4.5 in the FTIR Protocol).

3.9 One hundred percent line. A double beam transmittance spectrum obtained by combining two successive background single beam spectra. Ideally, this line is equal to 100 percent transmittance (or zero absorbance) at every point in the spectrum. The zero absorbance line is used to measure the RMS noise of the system.

3.10 Background Deviation. Any deviation (from 100 percent) in the one hundred percent line (or from zero absorbance). Deviations greater than ± 5 percent in any analytical region are unacceptable. Such deviations indicate a change in the instrument throughput relative to the single-beam background.

3.11 Batch Sampling. A gas cell is alternately filled and evacuated. A Spectrum of each filled cell (one discrete sample) is collected and saved.

3.12 Continuous Sampling. Sample is continuously flowing through a gas cell. Spectra of the flowing sample are collected at regular intervals.

3.13 Continuous Operation. In continuous operation an FTIR CEM system, without user intervention, samples flue gas, records spectra of samples, saves the spectra to a disk, analyzes the spectra for the target analytes, and prints concentrations of target analytes to a computer file. User intervention is permitted for initial set-up of sampling system, initial calibrations, and periodic maintenance.

3.14 Sampling Time. In batch sampling—the time required to fill the cell with flue gas. In continuous sampling—the time required to collect the infrared spectrum of the sample gas.

3.15 PPM-Meters. Sample concentration expressed as the concentration-path length product, ppm (molar) concentration multiplied by the path length of the FTIR gas cell. Expressing concentration in these units provides a way to directly compare measurements made using systems with different optical configurations. Another useful expression is (ppm-meters)/K, where K is the absolute temperature of the sample in the gas cell.

3.16 CEM Measurement Time Constant. The Time Constant (TC, minutes for one cell volume to flow through the cell) determines the minimum interval for complete removal of an analyte from the FTIR cell. It depends on the sampling rate (R_s in Lpm), the FTIR cell volume (V_{cell} in L) and the chemical and physical properties of an analyte.

$$TC = \frac{V_{cell}}{R_s} \quad (1)$$

For example, if the sample flow rate (through the FTIR cell) is 5 Lpm and the cell volume is 7 liters, then TC is equal to 1.4 minutes (0.71 cell volumes per minute). This performance specification defines $5 * TC$ as the minimum interval between independent samples.

3.17 Independent Measurement. Two independent measurements are spectra of two independent samples. Two independent samples are separated by, at least 5 cell volumes. The interval between independent measurements depends on the cell volume and the sample flow rate (through the cell). There is no mixing of gas between two independent samples. Alternatively, estimate the analyte residence time empirically: (1) Fill cell to ambient pressure with a (known analyte concentration) gas standard, (2) measure the spectrum of the gas standard, (3) purge the cell with zero gas at the sampling rate and collect a spectrum every minute until the analyte standard is no longer detected spectroscopically. If the measured time corresponds to less than 5 cell volumes, use $5 * TC$ as the minimum interval between independent measurements. If the measured time is greater than $5 * TC$, then use this time as the minimum interval between independent measurements.

3.18 Test Condition. A period of sampling where all process, and sampling conditions, and emissions remain constant and during which a single sampling technique and a single analytical program are used. One Run may include results for more than one test condition. Constant emissions means that the composition of the emissions remains approximately stable so that a single analytical program is suitable for analyzing all of the sample spectra. A greater than two-fold change in analyte or interferant concentrations or the appearance of additional compounds in the emissions, may constitute a new test condition and may require modification of the analytical program.

3.19 Run. A single Run consists of spectra (one spectrum each) of at least 10 independent samples over a minimum of one hour. The concentration results from the spectra can be averaged together to give a run average for each analyte measured in the test run.

4.0 Interferences. Several compounds, including water, carbon monoxide, and carbon dioxide, are known interferences in the infrared region in which the FTIR instrument operates. Follow the procedures in the FTIR protocol for subtracting or otherwise dealing with these and other interferences.

5.0 Safety. The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification does not purport to address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. The CEMS users manual and

materials recommended by this performance specification should be consulted for specific precautions to be taken.

6.0 Equipment and Supplies. 6.1 Installation of sampling equipment should follow requirements of FTIR test Methods such as references 1 and 3 and the EPA FTIR Protocol (reference 2). Select test points where the gas stream composition is representative of the process emissions. If comparing to a reference method, the probe tips for the FTIR CEM and the RM should be positioned close together using the same sample port if possible.

6.2 FTIR Specifications. The FTIR CEM must be equipped with reference spectra bracketing the range of path length-concentrations (absorbance intensities) to be measured for each analyte. The effective concentration range of the analyzer can be adjusted by changing the path length of the gas cell or by diluting the sample. The optical configuration of the FTIR system must be such that maximum absorbance of any target analyte is no greater than 1.0 and the minimum absorbance of any target analyte is at least 10 times the RMSD noise in the analytical region. For example, if the measured RMSD in an analytical region is equal to 10^{-3} , then the peak analyte absorbance is required to be at least 0.01. Adequate measurement of all of the target analytes may require changing path lengths during a run, conducting separate runs for different analytes, diluting the sample, or using more than one gas cell.

6.3 Data Storage Requirements. The system must have sufficient capacity to store all data collected in one week of routine sampling. Data must be stored to a write-protected medium, such as write-once-read-many (WORM) optical storage medium or to a password protected remote storage location. A back-up copy of all data can be temporarily saved to the computer hard drive. The following items must be stored during testing.

- At least one sample interferogram per sampling Run or one interferogram per hour, whichever is greater. This assumes that no sampling or analytical conditions have changed during the run.
- All sample absorbance spectra (about 12 per hr, 288 per day).
- All background spectra and interferograms (variable, but about 5 per day).
- All CTS spectra and interferograms (at least 2 each 24 hour period).
- Documentation showing a record of resolution, path length, apodization, sampling time, sampling conditions, and test conditions for all sample, CTS, calibration, and background spectra.

Using a resolution of 0.5 cm^{-1} , with analytical range of 3500 cm^{-1} , assuming about 65 Kbytes per spectrum and 130 Kb per interferogram, the storage requirement is about 164 Mb for one week of continuous sampling. Lower spectral resolution requires less storage capacity. All of the above data must be stored for at least two weeks. After two weeks, storage requirements include: (1) All analytical results (calculated concentrations), (2) at least 1 sample spectrum with corresponding background and sample interferograms for each test

condition, (3) CTS and calibration spectra with at least one interferogram for CTS and all interferograms for calibrations, (4) a record of analytical input used to produce results, and (5) all other documentation. These data must be stored according to the requirements of the applicable regulation.

7.0 Reagents and Standards. [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport. [Reserved]

9.0 Quality Control. These procedures shall be used for periodic quarterly or semiannual QA/QC checks on the operation of the FTIR CEM. Some procedures test only the analytical program and are not intended as a test of the sampling system.

9.1 Audit Sample. This can serve as a check on both the sampling system and the analytical program.

9.1.1 Sample Requirements. The audit sample can be a mixture or a single component. It must contain target analyte(s) at approximately the expected flue gas concentration(s). If possible, each mixture component concentration should be NIST traceable (± 2 percent accuracy). If a cylinder mixture standard(s) cannot be obtained, then, alternatively, a gas phase standard can be generated from a condensed phase analyte sample. Audit sample contents and concentrations are not revealed to the FTIR CEM operator until after successful completion of procedures in 5.3.2.

9.1.2 Test Procedure. An audit sample is obtained from the Administrator. Spike the audit sample using the analyte spike procedure in Section 11. The audit sample is measured directly by the FTIR system (undiluted) and then spiked into the effluent at a known dilution ratio. Measure a series of spiked and unspiked samples using the same procedures as those used to analyze the stack gas. Analyze the results using Sections 12.1 and 12.2. The measured concentration of each analyte must be within ± 5 percent of the expected concentration (plus the uncertainty), i.e., the calculated correction factor must be within 0.93 and 1.07 for an audit with an analyte uncertainty of ± 2 percent.

9.2 Audit Spectra. Audit spectra can be used to test the analytical program of the FTIR CEM, but provide no test of the sampling system.

9.2.1 Definition and Requirements. Audit spectra are absorbance spectra that: (1) Have been well characterized, and (2) contain absorbance bands of target analyte(s) and potential interferants at intensities equivalent to what is expected in the source effluent. Audit spectra are provided by the administrator without identifying information. Methods of preparing Audit spectra include: (1) Mathematically adding sample spectra or adding reference and interferant spectra, (2) obtaining sample spectra of mixtures prepared in the laboratory, or (3) they may be sample spectra collected previously at a similar source. In the last case it must be demonstrated that the analytical results are correct and reproducible. A record associated with each Audit spectrum documents its method of preparation. The documentation must be sufficient to enable an independent analyst to reproduce the Audit spectra.

9.2.2 Test Procedure. Audit spectra concentrations are measured using the FTIR CEM analytical program. Analytical results must be within ± 5 percent of the certified audit concentration for each analyte (plus the uncertainty in the audit concentration). If the condition is not met, demonstrate how the audit spectra are unrepresentative of the sample spectra. If the audit spectra are representative, modify the FTIR CEM analytical program until the test requirement is met. Use the new analytical program in subsequent FTIR CEM analyses of effluent samples.

9.3 Submit Spectra For Independent Analysis. This procedure tests only the analytical program and not the FTIR CEM sampling system. The analyst can submit FTIR CEM spectra for independent analysis by EPA. Requirements for submission include: (1) Three representative absorbance spectra (and stored interferograms) for each test period to be reviewed, (2) corresponding CTS spectra, (3) corresponding background spectra and interferograms, (4) spectra of associated spiked samples if applicable, and (5) analytical results for these sample spectra. The analyst will also submit documentation of process times and conditions, sampling conditions associated with each spectrum, file names and sampling times, method of analysis and reference spectra used, optical configuration of FTIR CEM including cell path length and temperature, spectral resolution and apodization used for every spectrum. Independent analysis can also be performed on site in conjunction with the FTIR CEM sampling and analysis. Sample spectra are stored on the independent analytical system as they are collected by the FTIR CEM system. The FTIR CEM and the independent analyses are then performed separately. The two analyses will agree to within ± 20 percent for each analyte using the procedure in Section 12.3. This assumes both analytical routines have properly accounted for differences in optical path length, resolution, and temperature between the sample spectra and the reference spectra.

10.0 Calibration/Standardization.

10.1 Calibration Transfer Standards. For CTS requirements see Section 4.5 of the FTIR Protocol. A well characterized absorbance band in the CTS gas is used to measure the path length and line resolution of the instrument. The CTS measurements made at the beginning of every 24 hour period must agree to within ± 5 percent after correction for differences in pressure. Verify that the frequency response of the instrument and CTS absorbance intensity are correct by comparing to other CTS spectra or by referring to the literature.

10.2 Analyte Calibration. If EPA library reference spectra are not available, use calibration standards to prepare reference spectra according to Section 6 of the FTIR Protocol. A suitable set of analyte reference data includes spectra of at least 2 independent samples at each of at least 2 different concentrations. The concentrations bracket a range that includes the expected analyte absorbance intensities. The linear fit of the reference analyte band areas must have a fractional calibration uncertainty (FCU in Appendix F of the FTIR Protocol) of no

greater than 10 percent. For requirements of analyte standards refer to Section 4.6 of the FTIR Protocol.

10.3 System Calibration. The calibration standard is introduced at a point on the sampling probe. The sampling system is purged with the calibration standard to verify that the absorbance measured in this way is equal to the absorbance in the analyte calibration. Note that the system calibration gives no indication of the ability of the sampling system to transport the target analyte(s) under the test conditions.

10.4 Analyte Spike. The target analyte(s) is spiked at the outlet of the sampling probe, upstream of the particulate filter, and combined with effluent at a ratio of about 1 part spike to 9 parts effluent. The measured absorbance of the spike is compared to the expected absorbance of the spike plus the analyte concentration already in the effluent. This measures sampling system bias, if any, as distinguished from analyzer bias. It is important that spiked sample pass through all of the sampling system components before analysis.

10.5 Signal-to-Noise Ratio (S/N). The measure of S/N in this performance specification is the root-mean-square (RMS) noise level as given in Appendix C of the FTIR Protocol. The RMS noise level of a contiguous segment of a spectrum is defined as the RMS difference (RMSD) between the n contiguous absorbance values (A_i) which form the segment and the mean value (A_M) of that segment.

$$\text{RMSD} = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^n (A_i - A_M)^2} \quad (2)$$

A decrease in the S/N may indicate a loss in optical throughput, or detector or interferometer malfunction.

10.6 Background Deviation. The 100 percent baseline must be between 95 and 105 percent transmittance (absorbance of 0.02 to -0.02) in every analytical region. When background deviation exceeds this range, a new background spectrum must be collected using nitrogen or other zero gas.

10.7 Detector Linearity. Measure the background and CTS at three instrument aperture settings; one at the aperture setting to be used in the testing, and one each at settings one half and twice the test aperture setting. Compare the three CTS spectra. CTS band areas should agree to within the uncertainty of the cylinder standard. If test aperture is the maximum aperture, collect CTS spectrum at maximum aperture, then close the aperture to reduce the IR throughput by half. Collect a second background and CTS at the smaller aperture setting and compare the spectra as above. Instead of changing the aperture neutral density filters can be used to attenuate the infrared beam. Set up the FTIR system as it will be used in the test measurements. Collect a CTS spectrum. Use a neutral density filter to attenuate the infrared beam (either immediately after the source or the interferometer) to approximately $1/2$ its original intensity. Collect a second CTS spectrum. Use another filter to attenuate the infrared beam to approximately $1/4$ its original intensity. Collect a third background

and CTS spectrum. Compare the CTS spectra as above. Another check on linearity is to observe the single beam background in frequency regions where the optical configuration is known to have a zero response. Verify that the detector response is "flat" and equal to zero in these regions. If detector response is not linear, decrease aperture, or attenuate the infrared beam. Repeat the linearity check until system passes the requirement.

11.0 Analytical Procedure.

11.1 Initial Certification. First, perform the evaluation procedures in Section 6.0 of the FTIR Protocol. The performance of an FTIR CEM can be certified upon installation using EPA Method 301 type validation (40 CFR, Part 63, Appendix A), or by comparison to a reference Method if one exists for the target analyte(s). Details of each procedure are given below. Validation testing is used for initial certification upon installation of a new system. Subsequent performance checks can be performed with more limited analyte spiking. Performance of the analytical program is checked initially, and periodically as required by EPA, by analyzing audit spectra or audit gases.

11.1.1 Validation. Use EPA Method 301 type sampling (reference 4, Section 5.3 of Method 301) to validate the FTIR CEM for measuring the target analytes. The analyte spike procedure is as follows: (1) A known concentration of analyte is mixed with a known concentration of a non-reactive tracer gas, (2) the undiluted spike gas is sent directly to the FTIR cell and a spectrum of this sample is collected, (3) pre-heat the spiked gas to at least the sample line temperature, (4) introduce spike gas at the back of the sample probe upstream of the particulate filter, (5) spiked effluent is carried through all sampling components downstream of the probe, (6) spike at a ratio of roughly 1 part spike to 9 parts flue gas (or more dilute), (7) the spike-to-flue gas ratio is estimated by comparing the spike flow to the total sample flow, and (8) the spike ratio is verified by comparing the tracer concentration in spiked flue gas to the tracer concentration in undiluted spike gas. The analyte flue gas concentration is unimportant as long as the spiked component can be measured and the sample matrix (including interferences) is similar to its composition under test conditions. Validation can be performed using a single FTIR CEM analyzing sample spectra collected sequentially. Since flue gas analyte (unspiked) concentrations can vary, it is recommended that two separate sampling lines (and pumps) are used; one line to carry unspiked flue gas and the other line to carry spiked flue gas. Even with two sampling lines the variation in unspiked concentration may be fast compared to the interval between consecutive measurements. Alternatively, two FTIR CEMs can be operated side-by-side, one measuring spiked sample, the other unspiked sample. In this arrangement spiked and unspiked measurements can be synchronized to minimize the affect of temporal variation in the unspiked analyte concentration. In either sampling arrangement, the interval between measured concentrations used in the statistical analysis

should be, at least, 5 cell volumes ($5 \times TC$ in equation 1). A validation run consists of, at least, 24 independent analytical results, 12 spiked and 12 unspiked samples. See Section 3.17 for definition of an "independent" analytical result. The results are analyzed using Sections 12.1 and 12.2 to determine if the measurements passed the validation requirements. Several analytes can be spiked and measured in the same sampling run, but a separate statistical analysis is performed for each analyte. In lieu of 24 independent measurements, averaged results can be used in the statistical analysis. In this procedure, a series of consecutive spiked measurements are combined over a sampling period to give a single average result. The related unspiked measurements are averaged in the same way. The minimum 12 spiked and 12 unspiked result averages are obtained by averaging measurements over subsequent sampling periods of equal duration. The averaged results are grouped together and statistically analyzed using Section 12.2.

11.1.1.1 Validation with a Single Analyzer and Sampling Line. If one sampling line is used, connect the sampling system components and purge the entire sampling system and cell with at least 10 cell volumes of sample gas. Begin sampling by collecting spectra of 2 independent unspiked samples. Introduce the spike gas into the back of the probe, upstream of the particulate filter. Allow 10 cell volumes of spiked flue gas to purge the cell and sampling system. Collect spectra of 2 independent spiked samples. Turn off the spike flow and allow 10 cell volumes of unspiked flue gas to purge the FTIR cell and sampling system. Repeat this procedure 6 times until the 24 samples are collected. Spiked and unspiked samples can also be measured in groups of 4 instead of in pairs. Analyze the results using Sections 12.1 and 12.2. If the statistical analysis passes the validation criteria, then the validation is completed. If the results do not pass the validation, the cause may be that temporal variations in the analyte sample gas concentration are fast relative to the interval between measurements. The difficulty may be avoided by: (1) Averaging the measurements over long sampling periods and using the averaged results in the statistical analysis, (2) modifying the sampling system to reduce TC by, for example, using a smaller volume cell or increasing the sample flow rate, (3) using two sample lines (4) use two analyzers to perform synchronized measurements. This performance specification permits modifications in the sampling system to minimize TC if the other requirements of the validation sampling procedure are met.

11.1.1.2 Validation With a Single Analyzer and Two Sampling Lines. An alternative sampling procedure uses two separate sample lines, one carrying spiked flue gas, the other carrying unspiked gas. A valve in the gas distribution manifold allows the operator to choose either sample. A short heated line connects the FTIR cell to the 3-way valve in the manifold. Both sampling lines are continuously purged. Each sample line has a rotameter and a bypass vent line after the rotameter, immediately upstream of the valve, so that the spike and unspiked

sample flows can each be continuously monitored. Begin sampling by collecting spectra of 2 independent unspiked samples. Turn the sampling valve to close off the unspiked gas flow and allow the spiked flue gas to enter the FTIR cell. Isolate and evacuate the cell and fill with the spiked sample to ambient pressure. (While the evacuated cell is filling, prevent air leaks into the cell by making sure that the spike sample rotameter always indicates that a portion of the flow is directed out the by-pass vent.) Open the cell outlet valve to allow spiked sample to continuously flow through the cell. Measure spectra of 2 independent spiked samples. Repeat this procedure until at least 24 samples are collected.

11.1.1.3 Synchronized Measurements With Two Analyzers. Use two FTIR analyzers, each with its own cell, to perform synchronized spiked and unspiked measurements. If possible, use a similar optical configuration for both systems. The optical configurations are compared by measuring the same CTS gas with both analyzers. Each FTIR system uses its own sampling system including a separate sampling probe and sampling line. A common gas distribution manifold can be used if the samples are never mixed. One sampling system and analyzer measures spiked effluent. The other sampling system and analyzer measures unspiked flue gas. The two systems are synchronized so that so that each measures spectra at approximately the same times. The sample flow rates are also synchronized so that both sampling rates are approximately the same ($TC1 \sim TC2$ in equation 1). Start both systems at the same time. Collect spectra of at least 12 independent samples with each (spiked and unspiked) system to obtain the minimum 24 measurements. Analyze the analytical results using Sections 12.1 and 12.2. Run averages can be used in the statistical analysis instead of individual measurements.

11.1.1.4 Compare to a Reference Method (RM). Obtain EPA approval that the method qualifies as an RM for the analyte(s) and the source to be tested. Follow the published procedures for the RM in preparing and setting up equipment and sampling system, performing measurements, and reporting results. Since FTIR CEMS have multicomponent capability, it is possible to perform more than one RM simultaneously, one for each target analyte. Conduct at least 9 runs where the FTIR CEM and the RM are sampling simultaneously. Each Run is at least 30 minutes long and consists of spectra of at least 5 independent FTIR CEM samples and the corresponding RM measurements. If more than 9 runs are conducted, the analyst may eliminate up to 3 runs from the analysis if at least 9 runs are used.

11.1.1.4.1 RMs Using Integrated Sampling. Perform the RM and FTIR CEM sampling simultaneously. The FTIR CEM can measure spectra as frequently as the analyst chooses (and should obtain measurements as frequently as possible) provided that the measurements include spectra of at least 5 independent measurements every 30 minutes. Concentration results from all of the FTIR CEM spectra within a run may be averaged for use in the statistical comparison

even if all of the measurements are not independent. When averaging the FTIR CEM concentrations within a run, it is permitted to exclude some measurements from the average provided the minimum of 5 independent measurements every 30 minutes are included: The Run average of the FTIR CEM measurements depends on both the sample flow rate and the measurement frequency (MF). The run average of the RM using the integrated sampling method depends primarily on its sampling rate. If the target analyte concentration fluctuates significantly, the contribution to the run average of a large fluctuation depends on the sampling rate and measurement frequency, and on the duration and magnitude of the fluctuation. It is, therefore, important to carefully select the sampling rate for both the FTIR CEM and the RM and the measurement frequency for the FTIR CEM. The minimum of 9 run averages can be compared according to the relative accuracy test procedure in Performance Specification 2 for SO₂ and NO_x CEMs (40 CFR part 60, Appendix B).

11.1.1.4.2 *RMs Using a Grab Sampling Technique.* Synchronize the RM and FTIR CEM measurements as closely as possible. For a grab sampling RM record the volume collected and the exact sampling period for each sample. Synchronize the FTIR CEM so that the FTIR measures a spectrum of a similar cell volume at the same time as the RM grab sample was collected. Measure at least 5 independent samples with both the FTIR CEM and the RM for each of the minimum 9 Runs. Compare the Run concentration averages by using the relative accuracy analysis procedure in 40 CFR part 60, Appendix B.

11.1.1.4.3 *Continuous Emission Monitors (CEMs) as RMs.* If the RM is a CEM, synchronize the sampling flow rates of the RM and the FTIR CEM. Each run is at least 1-hour long and consists of at least 10 FTIR CEM measurements and the corresponding 10 RM measurements (or averages). For the statistical comparison use the relative accuracy analysis procedure in 40 CFR part 60, Appendix B. If the RM time constant is < 1/2 the FTIR CEM time constant, brief fluctuations in analyte concentrations which are not adequately measured with the slower FTIR CEM time constant can be excluded from the run average along with the corresponding RM measurements.

However, the FTIR CEM run average must still include at least 10 measurements over a 1-hr period. 12.0 *Calculations and Data Analysis.*

12.1 *Spike Dilution Ratio, Expected Concentration.* The Method 301 bias is calculated as follows.

$$B = S_m - M_m - CS$$

Where

B=Bias at the spike level

S_m=Mean of the observed spiked sample concentrations

M_m=Mean of the observed unspiked sample concentrations

CS=Expected value of the spiked concentration. The CS is determined by comparing the SF₆ tracer concentration in undiluted spike gas to the SF₆ tracer concentrations in the spiked samples;

$$DF = \frac{[SF_6]_{\text{direct}}}{[SF_6]_{\text{spiked}}} \quad (4)$$

The expected concentration (CS) is the measured concentration of the analyte in undiluted spike gas divided by the dilution factor

$$CS = \frac{[anal]_{\text{dir}}}{DF} \quad (5)$$

where

[anal]_{dir}=The analyte concentration in undiluted spike gas measured directly by filling the FTIR cell with the spike gas. If the bias is statistically significant (Section 12.2), Method 301 requires that a correction factor, CF, be multiplied by the analytical results, and that 0.7 ≤ CF ≤ 1.3.

$$CF = \frac{1}{1 + \frac{B}{CS}} \quad (6)$$

12.2 *Statistical Analysis of Validation Measurements.* Arrange the independent measurements (or measurement averages) as in Table 1. More than 12 pairs of measurements can be analyzed. The statistical analysis follows EPA Method 301, Section 6.3. Section 12.1 of this performance specification shows the calculations for the bias, expected spike concentration, and correction factor. This Section shows the determination of the statistical significance of the bias. Determine the statistical significance of the bias at the 95 percent confidence level by calculating the t-value for the set of measurements. First, calculate the differences, d_i, for each pair of spiked and each pair of unspiked measurements. Then calculate the standard deviation of the spiked pairs of measurements.

$$SD_s = \sqrt{\frac{\sum d_i^2}{2n}} \quad (7)$$

Where

d_i=The differences between pairs of spiked measurements.

SD_s=The standard deviation in the d_i values.

n=The number of spiked pairs, 2n=12 for the minimum of 12 spiked and 12 unspiked measurements.

Calculate the relative standard deviation, RSD, using SD_s and the mean of the spiked concentrations, S_m. The RSD must be ≤ 50%.

$$RSD = \left(\frac{SD}{S_m} \right) \quad (8)$$

Repeat the calculations in equations 7 and 8 to determine SD_u and RSD, respectively, for the unspiked samples.

Calculate the standard deviation of the mean using SD_s and SD_u from equation 7.

$$SD = \sqrt{SD_s^2 + SD_u^2} \quad (9)$$

The t-statistic is calculated as follows to test the bias for statistical significance:

$$t = \frac{|B|}{SBM} \quad (10)$$

Where the bias, B, and the correction factor, CF, are given in Section 12.1.

For 11 degrees of freedom, and a one-tailed distribution, Method 301 requires that t ≤ 2.201. If the t-statistic indicates the bias is statistically significant, then analytical measurements must be multiplied by the correction factor. There is no limitation on the number of measurements, but there must be at least 12 independent spiked and 12 independent unspiked measurements. Refer to the t-distribution (Table 2) at the 95 percent confidence level and appropriate degrees of freedom for the critical t-value. 13.0–15.0 [Reserved]

16.0 References.

1. Method 318, 40 CFR Part 63, Appendix A (Draft), "Measurement of Gaseous Formaldehyde, Phenol and Methanol Emissions by FTIR Spectroscopy," EPA Contract No. 68D20163, Work Assignment 2–18, February, 1995.

2. "EPA Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions from Stationary Industrial Sources," February, 1995.

3. "Measurement of Gaseous Organic and Inorganic Emissions by Extractive FTIR Spectroscopy," EPA Contract No. 68–D2–0165, Work Assignment 3–08.

4. "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 Part CFR 63, Appendix A.

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

TABLE 1.—ARRANGEMENT OF VALIDATION MEASUREMENTS FOR STATISTICAL ANALYSIS.

Measurement (or average)	Time	Spiked (ppm)	d _i spiked	Unspiked (ppm)	d _i unspiked
1	S ₁		U ₁	
2	S ₂	S ₂ –S ₁	U ₂	U ₂ –U ₁
3	S ₃		U ₃	
4	S ₄	S ₄ –S ₃	U ₄	U ₄ –U ₃