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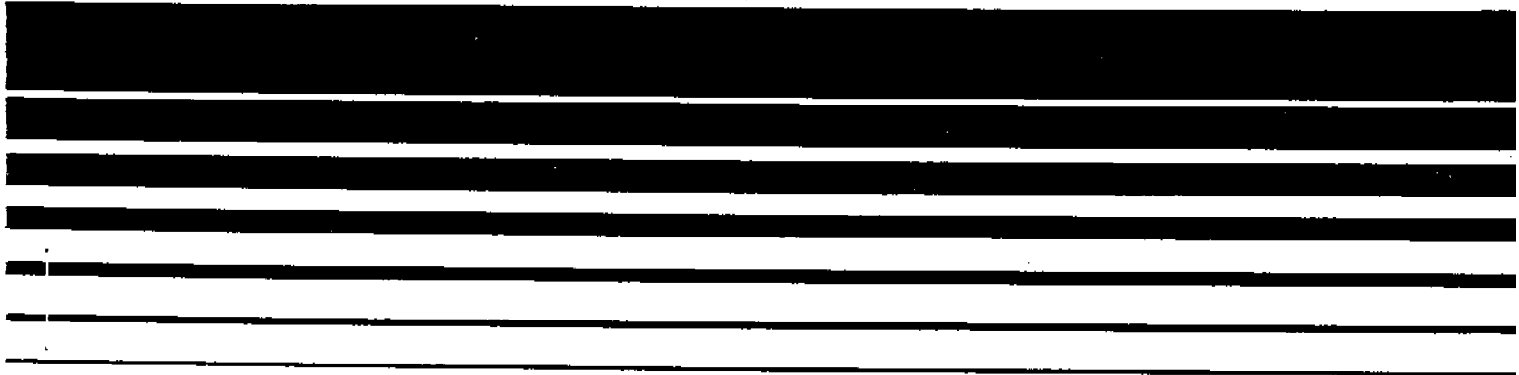
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# Guideline for PM<sub>10</sub> Episode Monitoring Methods



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# **Guideline for PM<sub>10</sub> Episode Monitoring Methods**

by

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## DISCLAIMER

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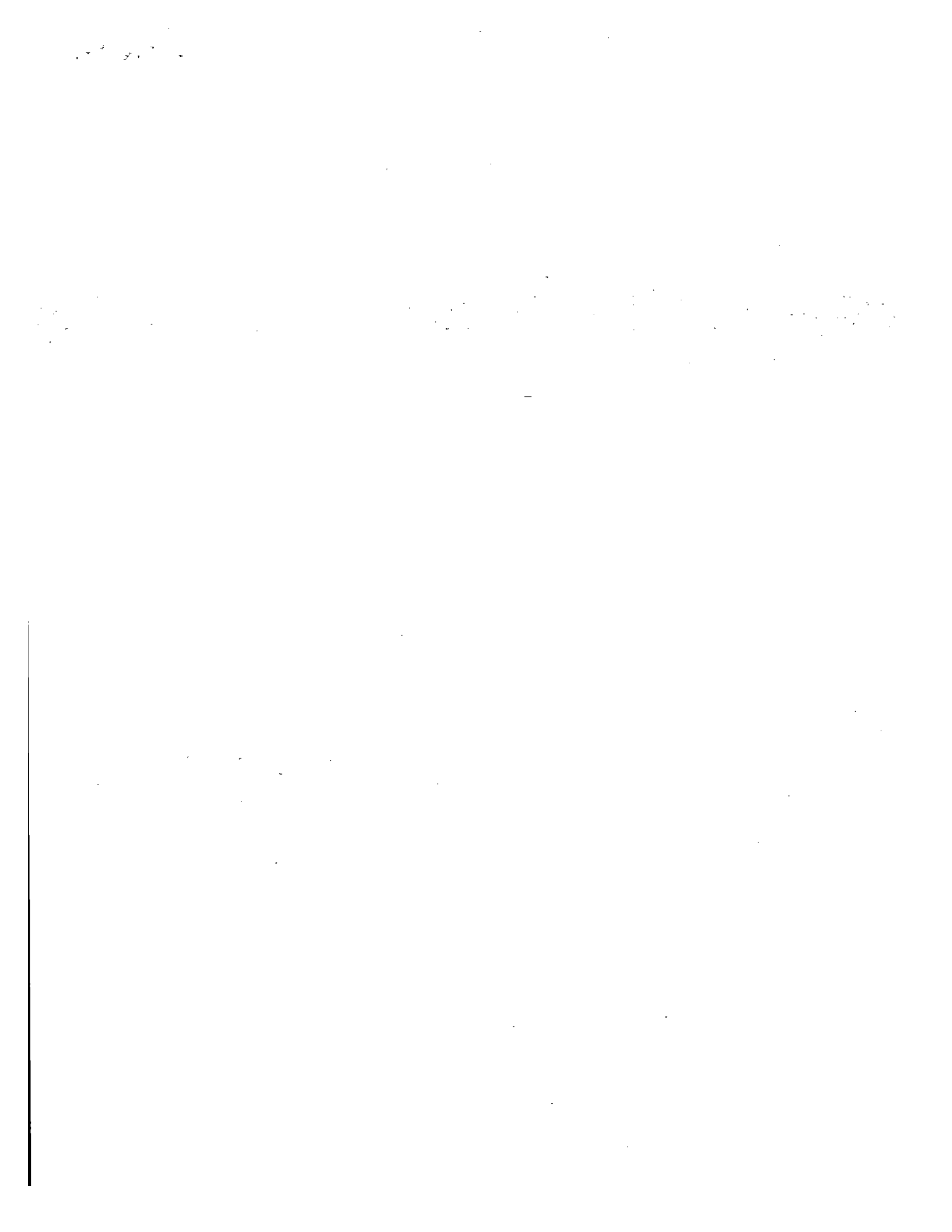
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## 1. INTRODUCTION

The EPA requirements which are prescribed in Title 40 Code of Federal Regulations (40 CFR) Part 58 for ambient air quality monitoring for purposes of State Implementation Plans (SIPs) have been revised, and include revisions to the emergency episode monitoring requirements now described in Appendix C of 40 CFR Part 58. The emergency episode guidance provided in Federal Regulation Part 51.16 and Appendix L are amended to reflect the new requirements. The new regulations permit the use of two modified versions of Appendix B of 40 CFR, Part 50 - Reference Method for the Determination of Particulate Matter in the Atmosphere. The regulations also permit the use of nonreference methods provided that specific site relationships to the reference method have been determined and documented and that these methods provide for short-term measurements.

### 1.1 Purpose and Scope

The procedures specified in the reference method are for a 24-hour sample collection period and a 24-hour equilibrium period before weighing. Therefore, the use of the reference method is not responsive to emergency episodes because of the 48-hour delay in determining the concentrations. During episode monitoring conditions, the concentrations must be available on a more current basis than provided for in the reference method for pollutant index calculations and/or corrective actions where necessary.

There are two purposes for this guideline. The first is to explain the principles of operation of the two episode particulate monitoring methods which are modifications of the reference method: (1) sampling over short

sampling time intervals; and (2) staggered sampling. These methods may be used by an agency in their particulate matter episode network without further testing in most cases.

Secondly, a procedure is described for establishing a site and season-specific relationship between the reference method and particulate methods other than the two mentioned above.

## 2. EPISODE MONITORING

The reference method for measurement of  $PM_{10}$  requires the use of an air sampler designed to pull air through a filter media in order to collect the entrained particles. The average concentration of  $PM_{10}$  collected over a 24-hour period is calculated by determining the mass of the particles collected and dividing the mass by the volume of air sampled. Appendix A provides information on the key topics that are included in the text of the  $PM_{10}$  reference method.

Two approaches recommended for episode monitoring require modifications to the reference method in order to reduce the time from the start of the sampling period to the reporting of the concentration results and/or to reduce the time between subsequent measurements at the same sampling location. One approach uses short sampling intervals, and the other uses staggered sampling intervals. Both methods rely on greatly reduced equilibration time for the filter moisture content.

### 2.1 Staggered Sampling

Staggered  $PM_{10}$  sampling is a method that provides the opportunity to update the information system at intervals more frequently than every 24 hours, but involves a short period for equilibration for the  $PM_{10}$  filters. The method requires the use of multiple monitors at the site. Operationally, the method involves staggered starting of the  $PM_{10}$  samplers at a constant time interval, running the sampler for 24 hours, then allowing the filter to equilibrate for 2 hours before determining the final weight of the filter. As an example, if it is determined that an update of the  $PM_{10}$  concentration is required every 4 hours, six  $PM_{10}$  samplers would be necessary.



Samplers would be started at 4-hour intervals after the first one is started. Twenty-four hours after the first sampler is started, the filter from that sampler is removed, equilibrated for 2 hours, then weighed and the PM<sub>10</sub> concentration determined; hence, the first concentration is determined approximately 26 hours after the start of sampling, then an updated concentration is available and the facilities available to accommodate multiple samplers, the PM<sub>10</sub> concentration can be updated at any desired time increment. More than six samplers at one site are probably not practical; consequently, increments of 4 hours are the shortest practical interval.

Some obvious precautions to be made when employing multiple samplers include arrangement of the samplers so they sample the same atmosphere but do not interfere with each other when operating simultaneously. Operation of a number of samplers will also require an electrical power supply capable of operating the samplers simultaneously without appreciably affecting the voltage as samplers turn on and turn off.

The principal advantages of staggered PM<sub>10</sub> sampling are obvious:

- o Rigorous performance testing is not required for implementation, because it is primarily based on the reference method.
- o The method is compatible with analytical facilities dedicated to the reference method.
- o Relatively rapid data reporting promotes a near real-time basis for contingency plan response and public information.

However, staggered PM<sub>10</sub> sampling is not without disadvantages when compared with the reference method. For discussion purposes, these disadvantages are separated into, (1) predictable shortcomings and (2) uncertainties. Predictable shortcomings are those problems that can be assessed prior to implementation. They include the following:

- o Increased demands of equipment, expendable inventory, electrical power, and labor may place an unacceptable strain on monitoring resources.
- o The physical aspects of the monitoring site may preclude acceptable siting of multiple samplers.
- o Data from the initial sample will not be available for 26 hours after the sampling start time.

The principal area of uncertainty that cannot be properly assessed prior to implementation lies in the shortened filter equilibration period. Equilibration is necessary to standardize the moisture condition of the filter/sample matrix so that inferred sample mass is not unduly biased by retained moisture. Moisture retention arises from two processes: hygroscopicity (differential absorption of water vapor onto hydrophilic materials) and retention of unbound moisture (i.e., water droplets sampled as if they were  $PM_{10}$ ).

Problems associated with hygroscopicity can be suppressed by using nonhygroscopic filtration material, but in many cases chemical and physical properties of the particles must be accounted for.

## 2.2 Short-Time Interval Sampling

With this method, an abbreviated sampling period and filter equilibration period are used. A 4-hour sample period followed by a 2-hour filter equilibration is suggested for a reasonable sampling duration. The short-time interval sampling method requires that a clean tared filter be installed on the sampler after every 4-hour sampling period. After removal from the sampler, the filter is conditioned in a dessicator for 2 hours, then weighed. The  $PM_{10}$  concentration can be determined 6 hours after starting the sample. Trends of  $PM_{10}$  concentrations can be determined if

at least four successive sample values indicate changes in the same direction.

The obvious advantage to using the short-time interval is the opportunity for quicker results from the start of sampling; hence, it is more representative of the most recent conditions and only one sampler is required (compared with six samplers needed for the staggered-sampling scheme). The filter and sample may be less subject to errors introduced, due to the abbreviated equilibration time when compared with the staggered-sampling method.

Some disadvantages that should be considered in conjunction with the short-time samples include the following:

- o A larger bias in the  $PM_{10}$  concentration may occur due to artifact particle formation on the filters. (Bias, due to artifact particle formation, will be reduced with proper selection of filter material, e.g., by use of quartz or Teflon filters.)
- o The possibility for human error is greater due to the increased number of filter changes required.
- o The average of six 4-hour concentration values is only an estimate of the true 24-hour continuous sample value.

### 3. ALTERNATIVE TO THE REFERENCE METHOD

Atmospheric aerosols may be monitored or measured with instruments that use several principles for detection other than the reference method. The advantage of these other instruments is primarily that they provide real-time readout of atmospheric aerosol concentrations.

A disadvantage of using the nonreference technique is the necessity of developing a site-specific correlation of an alternative monitoring technique with the reference method.

#### 3.1 Establishing Acceptability

Alternative methods of PM<sub>10</sub> sampling may be acceptable if a site and season-specific relationship is established between the alternate method and the reference method. The guidance provided for establishing the relationship is adapted from similar requirements for TSP monitoring. The evaluation procedure requires simultaneous side-by-side sampling using the reference method and the candidate method. A comparison of at least 10 simultaneous samples (or sample periods) is required. The data resulting from the simultaneous samples are analyzed to determine if a useful statistical relationship exists that will allow the use of the alternate method. Details of the procedure for evaluating the acceptability of candidate methods are provided in Appendix B.

The correlation coefficient between the reference method and alternative method being compared should have a value of 0.85 or greater in order to accept the alternative method.

Several factors should be considered when collecting samples or analyzing data to determine the correlation of the measurement technique.

Among the factors to consider are the following:

- o Influences of seasonal variations
- o Influences from local sources
- o Wind direction

Siting factors and similar considerations are discussed in a companion guideline document--"Network Design and Optimum Site Exposure Criteria for Particulate Matter."

### 3.2 Alternative Methods

The leading methods that may be considered as alternatives to the reference method are discussed in the remainder of this section.

3.2.1 Soiling Index -- is a sampling method that has been used in air monitoring stations for many years and has been relied upon to determine the onset of TSP episodes. Soiling index is determined by using an automated tape sampler that draws sample air through a filter tape and then by evaluating the change in transmittance or reflectance of light through the spot on the filter where the sample was collected. The transmittance or reflectance of light is highly variable depending on the type of aerosol collected. The optical properties of the aerosol sampled must remain constant in order to develop a good correlation between mass concentration and light transmittance. Site-specific studies would have to be conducted to show the uniformity of aerosols sampled before an adequate correlation with the reference method could be developed.

Ragan et al. (1979) have reported finding excellent correlation between the fine particulate concentrations and COH values. Ragan's study included correlation of COH values (average of six 2-hour samples) compared against the concentration of fine particules collected on 12-hour samples using a

high-volume sampler equipped with an Andersen size-fractionating sample head. Total particle concentrations from the high-volume samplers were corrected to represent particles less than 15  $\mu\text{m}$ . Correlation coefficients for the concentrations from five stages of the size-fractionated samples ranged from 0.947 to 0.971. A regression analysis was run to establish a quantitative relationship between COH and fine particulate data. A good correlation was found in the instance reported, but the results cannot be legitimately transferred to other sites without establishing the relationship at each site.

3.2.2 Photometers and Transmissometers -- are included in this text primarily because they have been used experimentally to attempt to determine suspended particle concentrations. Aerosol measurement with optical techniques is most effective for particles that are about 2  $\mu\text{m}$  diameter or smaller, where the light effect is most pronounced. In transmissometers, particles in the light path attenuate a light beam and a signal responsive to the changes in light at the detector. Integrating nephelometers also depend on changes in light intensity as the detection principle; however, in the integrating nephelometer, scattered light is detected, rather than an attenuated light beam. Some success has been reported with correlating the atmospheric mass concentration and the response to the integrating nephelometer (Butcher 1972)

3.2.3 The Beta Guage -- operates on the principle of collecting particles on a filter media that is located over a beta particle emitter. As the particles are collected on the filter material, fewer beta particles penetrate the accumulated mass. A correlation between the attenuation of beta particles and the collected particle mass allows the instrument to

provide real-time indication of particle concentration. The typical sampling period for the beta gauge is 1 or 2 hours; hence, a series of samples must be averaged to obtain a value corresponding to a long-term samples using a PM<sub>10</sub> reference method. A continuously cycling measurement mode is available with a printer to record each sample result. Jaklevic et al. (1981), have reported the beta gauge method is equivalent in accuracy to gravimetric methods when proper attention is paid to instrument design and calibration procedures. The conclusion is based on a study that included comparison of data using the beta gauge, a dichotomous sampler, and a high volume sampler.

3.2.4 The Piezoelectric -- principle has been used in other instruments designed to sample airborne particles and automatically display or record a mass concentration, such as the piezobalance produced by TSI, Incorporated. The standard piezobalance is available with a 3.5 um particle diameter cutoff option, but the instrument can be ordered with particle selectors with cutpoint up to 10 um. The piezobalance operates using a piezoelectric quartz crystal that oscillates at a constant frequency under static conditions. As particles are collected on the detecting crystal, the frequency of the oscillations changes in respect to the mass of particles collected. The change in frequency is detected and compared with the frequency at the initiation of the sampling period, and a concentration is calculated at the end of a 2-minute sampling period. The concentration is displayed at the end of the sample period until the beginning of the next period. The piezobalance is available in a portable, manually operated version and a fixed-location, fully automated version that is capable of continuously cycling (i.e., sampling, data recording, and automated crystal cleaning).

The beta attenuation and the piezoelectric quartz crystal instruments provide the short-term sampling options that are desirable for episode monitoring. Some caveats must be recognized when considering the use of these instruments. The effect of the moisture collected in the sample is not compensated for by either instrument. The effect of moisture collection is likely to have a more significant effect on the piezoelectric instrument. Particle collection efficiencies of the instruments must also be evaluated. Although the instruments are considered to be useful for collecting particles up to 10 um aerodynamic diameter, ambient conditions may considerably alter the actual size of particles collected. Fairchild (1980) has evaluated both types of instruments and compared results with those from gravimetric sampling. The report indicates the instruments evaluated accurately sample particles with + 25 percent of the gravimetric concentration when four or more instrument readings were averaged. The report also stated that the piezoelectric quartz crystal collected particles greater than 6 um aerodynamic diameter with poor efficiency due to poor mechanical coupling with the quartz crystal.

3.2.5 TEOM-Tapered Element Oscillating Microbalance -- A report of a recently designed instrument to detect fine particles and determine the concentration after a 30 minute sampling period indicates the instrument may be useful for short-term measurement of fine particles. The instrument must undergo further development, but is to be commercially available. The TEOM works by collecting particles on a filter cartridge that is attached to the narrow end of hollow tapered tube. The wide end of the tube is attached to the instrument. The tapered tube oscillates during the sampling period, with frequency of the oscillation being accurately monitored.



Loading of particles in the filter cartridge causes a shift in the oscillation frequency, which is interpreted and translated into a concentration by a microprocessor.

The system that has been developed and reported on is equipped with a 2.5  $\mu\text{m}$  cutpoint cyclone preseparator, so the measurement relates to the fine aerosol portion of airborne particle mass. The TEOM can be operated for a long time period with printer output programmed on a 1/2- to 1-hour schedule. A heater element in the intake maintains a constant temperature of the incoming aerosol to provide frequency stability and minimize the effect of humidity on the measurement.

The TEOM is a new device that has not been proven in field use. The device reportedly has resolved difficulties that exist with the quartz crystal microbalance instruments.

### 3.3 Site- and Season-Specific Relationship

Any of the automated aerosol measurement units must be compared with the  $\text{PM}_{10}$  reference method to obtain a site and season-specific relationship before the measurements from the nonreference method can be accepted for episode monitoring. Guidance for developing the site and season-specific relationship is provided in Appendix B.

### 3.4 Operable Size Ranges for Particulate Instruments

The Lawrence Berkeley Laboratories (LBL) has compiled an inventory of the specifications and capabilities for a variety of air pollutant monitoring instruments. The LBL document describing particle-collecting or detecting instruments provides the following table, Table 1, to indicate possible combinations of instruments that will detect particles over a wide range of particle sizes. The instruments are described in generic terms, but the

**Table 1. The Operable Size Ranges of Practical Combinations of Size Classifiers and Sensors\*\*\***

*All numbers are the diameter, in microns, of a spherical particle with a density of 1.0 gram/cubic centimeter (from Ref. 17a).*

Particle Size Classifier	Concentration Sensing Technique						
	Mass			Optical			
	Beta Radiation Attenuation 0.01 - 100	Piezoelectric Quartz Crystal 0.01 - 20	Light Transmission 0.2 - 100	Photometry 0.2 - 50	Soiling Potential 0.2 - 50	Electrostatic Ion Capture and Attenuation 0.005 - 100	Nuclei Counter 0.001 - 0.05
<u>Aerodynamic</u>							
Impactor (0.2** - 30)	0.2* - 30	0.2* - 20	0.2 - 30	0.2 - 30	0.2 - 30	0.2 - 30	-
Cyclone (0.5 - 30)	0.5* - 30	0.5* - 20	0.5 - 30	0.5 - 30	0.5 - 30	0.5 - 30	-
Gravitational Elutriator (1.0 - 100)	1.0* - 100	1.0* - 20	1.0 - 100	1.0 - 50	1.0 - 50	1.0 - 100	-
Gravitational Sedimentation (1.0 - 50)	1.0* - 50	1.0* - 20	1.0 - 50	1.0 - 50	1.0 - 50	1.0 - 50	-
Electrostatic (0.005 - 0.6)	-	-	-	-	-	0.005 - 0.6	0.005 - 0.05
Brownian Diffusion (0.001 - 0.05)	-	-	-	-	-	-	0.001 - 0.05

\*Although this is the lowest size cutoff of the classifier, the sensor can detect smaller particles below this size cutoff, lumping them into one size range.

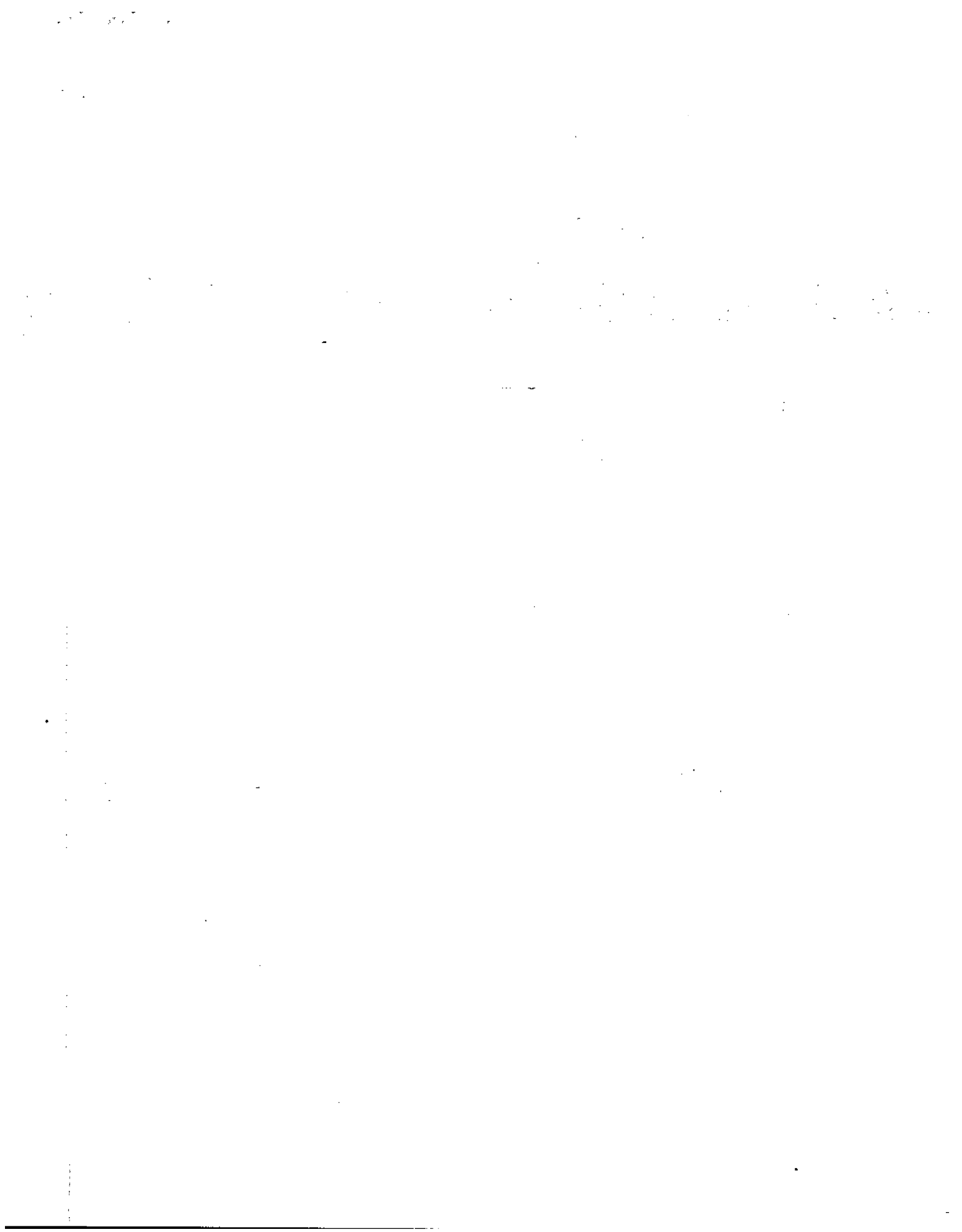
\*\*Low pressure impactor may prove useful down to 0.05 microns for some applications where volatile particles are not present.

\*\*\*This table is extracted in the form presented from Instrumentation for Environmental Monitoring AIR, LBL 1, Vol. 1, Part 2 Lawrence Berkeley Laboratory, University of California, Berkeley, Calif., 1975.

listing can give valuable guidance to possible instrument types that may be feasible for PM<sub>10</sub> episode monitoring.

#### 4. REFERENCES

1. Acton, F.S. 1959. Analysis of Straight-Line Data. New York: John Wiley and Sons.
2. Butcher, S.S., and Charlston, R.J. 1972. An Introduction to Air Chemistry. New York: Academic Press.
3. Fairchild, C.I.; Tillery, M.I., and Ettinger, H.J. 1980. An Evaluation of Fast Response Aerosol Mass Monitors. LA 8220, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.
4. Kramer, D.N., and Mitchel, P.W. 1967. Evaluation of Filters for High-Volume Sampling of Atmospheric Particulates. J. Am. Ind. Hyg. Assoc. (28)3:224-28.
5. Lewis, C.W. 1981. The Tapered Element Oscillating Microbalance: A Monitor for Short-Term Measurement of Fine Aerosol Mass Measurement. EPA Report 600/S2-81-146. Environmental Sciences Research Laboratory, Research Triangle Park, NC 27711.
6. Lippmann, M., Kleinman, M.T., and Bernstein, D.M. 1979. Size-Mass Distributions of the New York Summer Aerosol. Ann. N.Y. Acad. Sci. 322:29-44.
7. Natrella, M.G., ed. 1963. Experimental Statistics, Handbook 91. National Bureau of Standards, Washington, D.C.
8. Regan, G.F., Goranson, S.K., and Larson, L.L., 1979. Use of Tape Samplers as Fine Particulate Monitors. J. Air Pol. Control Assoc. (29) 1158-1160.
9. U.S. Environmental Protection Agency. 1979. Guidance for Selecting TSP Episode Monitoring Methods. EPA Report 450/4-79-007, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711.



## APPENDIX A

### REFERENCE METHOD FOR THE DETERMINATION OF PARTICULATE MATTER AS PM<sub>10</sub> IN THE ATMOSPHERE - Appendix J 40 CFR 50 (Reproduced as promulgated in the Federal Register)

#### 1.0 APPLICABILITY

1.1 This method provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM<sub>10</sub>) in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards for particulate matter specified in § 50.6 of this chapter. The measurement process is non-destructive, and the PM<sub>10</sub> sample can be subjected to subsequent physical or chemical analyses. Quality assurance procedures and guidance are provided in Part 58, Appendices A and B, of this chapter and in References 1 and 2.

#### 2.0 PRINCIPLE

2.1 An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM<sub>10</sub> size range. Each size fraction in the PM<sub>10</sub> size range is then collected on a separate filter over the specified sampling period. The particle size discrimination characteristics (sampling effectiveness and 50 percent cutpoint) of the sampler inlet are prescribed as performance specifications in Part 53 of this chapter.

2.2 Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM<sub>10</sub>. The total volume of air sampled, corrected to EPA reference conditions (24° C, 101.3 kPa), is determined from the measured flow rate and the sampling time. The mass concentration of PM<sub>10</sub> in the ambient air is computed as the total mass of collected particles in the PM<sub>10</sub> size range divided by the volume of air sampled, and is expressed in micrograms per standard cubic meter (ug/std m<sup>3</sup>). For PM<sub>10</sub> samples collected at temperatures and pressures significantly different from EPA reference conditions, these corrected concentrations sometimes differ substantially from actual concentrations (in micrograms per actual cubic meter), particularly at high elevations. Although not required, the actual PM<sub>10</sub> concentration can be calculated from the corrected concentration, using the average ambient temperature and barometric pressure during the sampling period.

2.3 A method based on this principle will be considered a reference method only if (a) the associated sampler meets the requirements specified in this appendix and the requirements in Part 53 of this chapter, and (b) the method has been designated as a reference method in accordance with Part 53 of this chapter.

### 3.0 RANGE

3.1 The lower limit of the mass concentration range is determined by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. For samplers having an automatic filter-changing mechanism, there may be no upper limit. For samplers that do not have an automatic filter-changing mechanism, the upper limit is determined by the filter mass loading beyond which the sampler no longer maintains the

operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, filter type, and perhaps other factors. Nevertheless, all samplers should be capable of measuring 24-hour  $PM_{10}$  mass concentrations of at least  $300 \text{ ug/std m}^3$  while maintaining the operating flow rate within the specified limits.

#### 4.0 PRECISION

4.1 The precision of  $PM_{10}$  samplers must be  $5 \text{ ug/m}^3$  for  $PM_{10}$  concentrations below  $80 \text{ ug/m}^3$  and 7 percent for  $PM_{10}$  concentrations above  $80 \text{ ug/m}^3$ , as required by Part 53 of this chapter, which prescribes a test procedure that determines the variation in the  $PM_{10}$  concentration measurements of identical samplers under typical sampling conditions. Continual assessment of precision via collocated samplers is required by Part 58 of this chapter for  $PM_{10}$  samplers used in certain monitoring networks.

#### 5.0 ACCURACY

5.1 Because the size of the particles making up ambient particulate matter varies over a wide range and the concentration of particles varies with particle size, it is difficult to define the absolute accuracy of  $PM_{10}$  samplers. Part 53 of this chapter provides a specification for the sampling effectiveness of  $PM_{10}$  samplers. This specification requires that the expected mass concentration calculated for a candidate  $PM_{10}$  sampler, when sampling a specified particle size distribution, be within  $\pm 10$  percent of that calculated for an ideal sampler whose sampling effectiveness is explicitly specified. Also, the particle size for 50 percent sampling effectiveness is required to



be  $10 \pm 0.5$  micrometers. Other specifications related to accuracy apply to flow measurement and calibration, filter media, analytical (weighing) procedures, and artifact. The flow rate accuracy of PM<sub>10</sub> samplers used in certain monitoring networks is required by Part 58 of this chapter to be assessed periodically via flow rate audits.

## 6.0 POTENTIAL SOURCES OF ERROR

6.1 Volatile Particles. Volatile particles collected on filters are often lost during shipment and/or storage of the filters prior to the post-sampling weighing<sup>3</sup>. Although shipment or storage of loaded filters is sometimes unavoidable, filters should be reweighed as soon as practical to minimize these losses.

6.2 Artifacts. Positive errors in PM<sub>10</sub> concentration measurements may result from retention of gaseous species on filters<sup>4,5</sup>. Such errors include the retention of sulfur dioxide and nitric acid. Retention of sulfur dioxide on filters, followed by oxidation to sulfate is referred to as artifact sulfate formation, a phenomenon which increases with increasing filter alkalinity<sup>6</sup>. Little or no artifact sulfate formation should occur using filters that meet the alkalinity specification in section 7.2.4. Artifact nitrate formation, resulting primarily from retention of nitric acid, occurs to varying degrees on many filter types, including glass fiber, cellulose ester, and many quartz fiber filters<sup>5,7,8,9,10</sup>. Loss of true atmospheric particulate nitrate during or following sampling may also occur due to dissociation or chemical reaction. This phenomenon has been observed on Teflon® filters<sup>8</sup> and inferred for quartz fiber filters<sup>11,12</sup>. The magnitude of nitrate artifact errors in PM<sub>10</sub> mass concentration measurements will vary with location and ambient temperature; however, for most sampling locations, these errors are expected to be small.

6.3 Humidity. The effects of ambient humidity on the sample are unavoidable. The filter equilibration procedure in section 9.0 is designed to minimize the effects of moisture on the filter medium.

6.4 Filter Handling. Careful handling of filters between presampling and postsampling weighings is necessary to avoid errors due to damaged filters or loss of collected particles from the filters. Use of a filter cartridge or cassette may reduce the magnitude of these errors. Filters must also meet the integrity specifications in section 7.2.3.

6.5 Flow Rate Variation. Variations in the sampler's operating flow rate may alter the particle size discrimination characteristics of the sampler inlet. The magnitude of this error will depend on the sensitivity of the inlet to variations in flow rate and on the particle distribution in the atmosphere during the sampling period. The use of a flow control device (section 7.1.3) is required to minimize this error.

6.6 Air Volume Determination. Errors in the air volume determination may result from errors in the flow rate and/or sampling time measurements. The flow control device serves to minimize errors in the flow rate determination, and an elapsed time meter (section 7.1.5) is required to minimize the error in the sampling time measurement.

## 7.0 APPARATUS

### 7.1 PM<sub>10</sub> Sampler

7.1.1 The sampler shall be designed to:

- a. Draw the air sample into the sampler inlet and through the particle collection filter at a uniform face velocity.

- b. Hold and seal the filter in a horizontal position so that sample air is drawn downward through the filter.
- c. Allow the filter to be installed and removed conveniently.
- d. Protect the filter and sampler from precipitation and prevent insects and other debris from being sampled.
- e. Minimize air leaks that would cause error in the measurement of the air volume passing through the filter.
- f. Discharge exhaust air at a sufficient distance from the sampler inlet to minimize the sampling of exhaust air.
- g. Minimize the collection of dust from the supporting surface.

7.1.2 The sampler shall have a sample air inlet system that, when operated within a specified flow rate range, provides particle size discrimination characteristics meeting all of the applicable performance specifications prescribed in Part 53 of this chapter. The sampler inlet shall show no significant wind direction dependence. The latter requirement can generally be satisfied by an inlet shape that is circularly symmetrical about a vertical axis.

7.1.3 The sampler shall have a flow control device capable of maintaining the sampler's operating flow rate within the flow rate limits specified for the sampler inlet over normal variations in line voltage and filter pressure drop.

7.1.4 The sampler shall provide a means to measure the total flow rate during the sampling period. A continuous flow recorder is recommended but not required. The flow rate device shall be accurate to  $\pm 2$  percent.

7.1.5 A timing/control device capable of starting and stopping the sampler shall be used to obtain a sample collection period of  $24 \pm 1$  hour ( $1,440 \pm 60$  min). An elapsed time meter, accurate to within  $\pm 15$  minutes, shall be used to measure sampling time. This meter is optional for samplers with continuous flow recorders if the sampling time measurement obtained by means of the recorder meets the  $\pm 15$  minute accuracy specification.

7.1.6 The sampler shall have an associated operation or instruction manual as required by Part 53 of this chapter which includes detailed instructions on the calibration, operation, and maintenance of the sampler.

## 7.2 Filters

7.2.1 Filter Medium. No commercially available filter medium is ideal in all respects for all samplers. The user's goals in sampling determine the relative importance of various filter characteristics (e.g., cost, ease of handling, physical and chemical characteristics, etc.) and, consequently, determine the choice among acceptable filters. Furthermore, certain types of filters may not be suitable for use with some samplers, particularly under heavy loading conditions (high mass concentrations), because of high or rapid increase in the filter flow resistance that would exceed the capability of the sampler's flow control device. However, samplers equipped with automatic filter-changing mechanisms may allow use of these types of filters. The specifications given below are minimum requirements to ensure acceptability of the filter medium for measurement of  $PM_{10}$  mass concentrations. Other filter evaluation criteria should be considered to meet individual sampling and analysis objectives.

7.2.2 Collection Efficiency. Defined as  $\geq 99$  percent, as measured by the DOP test (ASTM-2986) with 0.3  $\mu\text{m}$  particles at the sampler's operating face velocity.

7.2.3 Integrity. Defined as  $\pm 5 \text{ ug/m}^3$  (assuming sampler's nominal 24-hour air sample volume). Integrity is measured as the  $\text{PM}_{10}$  concentration equivalent corresponding to the average difference between the initial and the final weights of a random sample of test filters that are weighed and handled under actual or simulated sampling conditions, but have no air sample passed through them (i.e., filter blanks). As a minimum, the test procedure must include initial equilibration and weighing, installation on an inoperative sampler, removal from the sampler, and final equilibration and weighing.

7.2.4 Alkalinity. Defined as  $< 25$  microequivalents/gram of filter, as measured by the procedure given in Reference 13 following at least two months storage in a clean environment (free from contamination by acidic gases) at room temperature and humidity.

7.3 Flow Rate Transfer Standard. The flow rate transfer standard must be suitable for the sampler's operating flow rate and must be calibrated against a primary flow or volume standard that is traceable to the National Bureau of Standards (NBS). The flow rate transfer standard must be capable of measuring the sampler's operating flow rate with an accuracy of  $\pm 2$  percent.

#### 7.4 Filter Conditioning Environment

7.4.1 Temperature range:  $15^\circ$  to  $30^\circ$  C.

7.4.2 Temperature control:  $\pm 3^\circ$  C.

7.4.3 Humidity range: 20% to 45% RH.

7.4.4 Humidity control: + 5% RH.

7.5 Analytical Balance. The analytical balance must be suitable for weighing the type and size of filters required by the sampler. The range and sensitivity required will depend on the filter tare weights and mass loadings. Typically, an analytical balance with a sensitivity of 0.1 mg is required for high volume samplers (flow rates  $> 0.5 \text{ m}^3/\text{min}$ ). Lower volume samplers (flow rates  $< 0.5 \text{ m}^3/\text{min}$ ) will require a more sensitive balance.

## 8.0 CALIBRATION

### 8.1 General Requirements

8.1.1 Calibration of the sampler's flow measurement device is required to establish traceability of subsequent flow measurements to a primary standard. A flow rate transfer standard calibrated against a primary flow or volume standard shall be used to calibrate or verify the accuracy of the sampler's flow measurement device.

8.1.2 Particle size discrimination by inertial separation requires that specific air velocities be maintained in the sampler's air inlet system. Therefore, the flow rate through the sampler's inlet must be maintained throughout the sampling period within the design flow rate range specified by the manufacturer. Design flow rates are specified as actual volumetric flow rates, measured at existing conditions of temperature and pressure ( $Q_a$ ). In contrast, mass concentrations of  $\text{PM}_{10}$  are computed using flow rates corrected to EPA reference conditions of temperature and pressure ( $Q_{std}$ ).

### 8.2 Flow Rate Calibration Procedure

8.2.1  $\text{PM}_{10}$  samplers employ various types of flow control and flow measurement devices. The specific procedure used for flow rate calibration

or verification will vary depending on the type of flow controller and flow indicator employed. Calibration in terms of actual volumetric flow rates ( $Q_a$ ) is generally recommended, but other measures of flow rate (e.g.,  $Q_{std}$ ) may be used provided the requirements of section 8.1 are met. The general procedure given here is based on actual volumetric flow units ( $Q_a$ ) and serves to illustrate the steps involved in the calibration of a  $PM_{10}$  sampler. Consult the sampler manufacturer's instruction manual and Reference 2 for specific guidance on calibration. Reference 14 provides additional information on the use of the commonly used measures of flow rate and their interrelationships.

8.2.2 Calibrate the flow rate transfer standard against a primary flow or volume standard traceable to NBS. Establish a calibration relationship (e.g., an equation or family of curves) such that traceability to the primary standard is accurate to within 2 percent over the expected range of ambient conditions (i.e., temperatures and pressures) under which the transfer standard will be used. Recalibrate the transfer standard periodically.

8.2.3 Following the sampler manufacturer's instruction manual, remove the sampler inlet and connect the flow rate transfer standard to the sampler such that the transfer standard accurately measures the sampler's flow rate. Make sure there are no leaks between the transfer standard and the sampler.

8.2.4 Choose a minimum of three flow rates (actual  $m^3/min$ ), spaced over the acceptable flow rate range specified for the inlet (see 7.1.2) that can be obtained by suitable adjustment of the sampler flow rate. In accordance with the sampler manufacturer's instruction manual,

obtain or verify the calibration relationship between the flow rate (actual  $\text{m}^3/\text{min}$ ) as indicated by the transfer standard and the sampler's flow indicator response. Record the ambient temperature and barometric pressure. Temperature and pressure corrections to subsequent flow indicator readings may be required for certain types of flow measurement devices. When such corrections are necessary, correction on an individual or daily basis is preferable. However, seasonal average temperature and average barometric pressure for the sampling site may be incorporated into the sampler calibration to avoid daily corrections. Consult the sampler manufacturer's instruction manual and Reference 2 for additional guidance.

8.2.5 Following calibration, verify that the sampler is operating at its design flow rate (actual  $\text{m}^3/\text{min}$ ) with a clean filter in place.

8.2.6 Replace the sampler inlet.

## 9.0 PROCEDURE

9.1 The sampler shall be operated in accordance with the specific guidance provided in the sampler manufacturer's instruction manual and in Reference 2. The general procedure given here assumes that the sampler's flow rate calibration is based on flow rates at ambient conditions ( $Q_a$ ) and serves to illustrate the steps involved in the operation of a  $\text{PM}_{10}$  sampler.

9.2 Inspect each filter for pinholes, particles, and other imperfections. Establish a filter information record and assign an identification number to each filter.

9.3 Equilibrate each filter in the conditioning environment (see 7.4) for at least 24 hours.

9.4 Following equilibration, weigh each filter and record the presampling weight with the filter identification number.



9.11 Determine and record the average flow rate ( $\bar{Q}_a$ ) in actual  $m^3/min$  for the sampling period in accordance with the instructions provided in the sampler manufacturer's instruction manual. Record the elapsed time meter final reading and, if needed, the average ambient temperature and barometric pressure for the sampling period (see note following step 9.6).

9.12 Carefully remove the filter from the sampler, following the sampler manufacturer's instruction manual. Touch only the outer edges of the filter.

9.13 Place the filter in a protective holder or container (e.g., petri dish, glassine envelope, or manila folder).

9.14 Record any factors such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement on the filter information record.

9.15 Transport the exposed sample filter to the filter conditioning environment as soon as possible for equilibration and subsequent weighing.

9.16 Equilibrate the exposed filter in the conditioning environment for at least 24 hours under the same temperature and humidity conditions used for presampling filter equilibration (see 9.3).

9.17 Immediately after equilibration, reweigh the filter and record the postsampling weight with the filter identification number.

## 10.0 SAMPLER MAINTENANCE

10.1 The  $PM_{10}$  sampler shall be maintained in strict accordance with the maintenance procedures specified in the sampler manufacturer's instruction manual.

## 11.0 CALCULATIONS

11.1 Calculate the average flow rate over the sampling period corrected to EPA reference conditions as  $\bar{Q}_{std}$ . When the sampler's flow indicator is calibrated in actual volumetric units ( $Q_a$ ),  $\bar{Q}_{std}$  is calculated as:

$$\bar{Q}_{std} = \bar{Q}_a \times (P_{av}/T_{av})(T_{std}/P_{std})$$

where  $\bar{Q}_{std}$  = average flow rate at EPA reference conditions, std m<sup>3</sup>/min;

$\bar{Q}_a$  = average flow rate at ambient conditions, m<sup>3</sup>/min;

$P_{av}$  = average barometric pressure during the sampling period or average barometric pressure for the sampling site, kPa (or mm Hg);

$T_{av}$  = average ambient temperature during the sampling period or seasonal average ambient temperature for the sampling site, K;

$T_{std}$  = standard temperature, defined as 298 K;

$P_{std}$  = standard pressure, defined as 101.3 kPa (or 760 mm Hg).

11.2 Calculate the total volume of air sampled as:

$$V_{std} = \bar{Q}_{std} \times t$$

where  $V_{std}$  = total air sampled in standard volume units, std m<sup>3</sup>;

$t$  = sampling time, min.

11.3 Calculate the PM<sub>10</sub> concentration as:

$$PM_{10} = (W_f - W_i) \times 10^6 / V_{std}$$

where  $PM_{10}$  = mass concentration of PM<sub>10</sub>, ug/std m<sup>3</sup>;

$W_f, W_i$  = final and initial weights of filter collecting PM<sub>10</sub> particles, g;

$10^6$  = conversion of g to ug.

Note: If more than one size fraction in the PM<sub>10</sub> size range is collected by the sampler, the sum of the net weight gain by each collection filter [ $\sum (W_f - W_i)$ ] is used to calculate the PM<sub>10</sub> mass concentration.

## 12.0 REFERENCES

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles. EPA-600/9-76-005, March 1976. Available from CERI, ORD Publications, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268.
2. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods. EPA-600/4-77-027a, May 1977. Available from CERI, ORD Publications, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268.
3. Clement, R.E., and F.W. Karasek. Sample Composition Changes in Sampling and Analysis of Organic Compounds in Aerosols. *Int. J. Environ. Analyt. Chem.*, 7:109, 1979.
4. Lee, R.E., Jr., and J. Wagman. A Sampling Anomaly in the Determination of Atmospheric Sulfate Concentration. *Amer. Ind. Hyg. Assoc. J.*, 27:266, 1966.
5. Appel, R.B., S.M. Wall, J. Tokiwa, and M. Haik. Interface Effects in Sampling Particulate Nitrate in Ambient Air. *Atmos. Environ.*, 13:319, 1979.
6. Coutant, R.W. Effect of Environmental Variables on Collection of Atmospheric Sulfate. *Environ. Sci. Technol.*, 11:873, 1977.
7. Spicer, C.W., and P. Schumacher. Interference in Sampling Atmospheric Particulate Nitrate. *Atmos. Environ.*, 11:873, 1977.
8. Appel, B.R., Y. Tokiwa and M. Haik. Sampling of Nitrates in Ambient Air. *Atmos. Environ.*, 15:283, 1981.
9. Spicer, D.W., and P.M. Schumacher. Particulate Nitrate: Laboratory and Field Studies of Major Sampling Interferences. *Atmos. Environ.*, 13:543, 1979.
10. Appel, B.R. Private Communication, 1982.
11. Pierson, W.R., W.W. Brachaczek, T.J. Korniski, T.J. Truex, and J.W. Butler. Artifact Formation of Sulfate, Nitrate, and Hydrogen Ion on Backup Filters: Allegheny Mountain Experiment. *J. Air Pollut. Control Assoc.*, 30:30, 1980.
12. Dunwoody, C.L. Rapid Nitrate Loss from PM<sub>10</sub> Filters. *J. Air Pollut. Control Assoc.*, 36:817, 1986.
13. Harrell, R.M. Measuring the Alkalinity of Hi-Vol Air Filters. EMSL/RTP-SOP-QAD-534, October 1985. Available from the U.S. Environmental Protection Agency, EMSL/QAD, Research Triangle Park, North Carolina 27711.

14. Smith, F., P.S. Wohlschlegel, R.S.C. Rogers, and D.J. Mulligan. Investigation of Flow Rate Calibration Procedures Associated with the High Volume Method for Determination of Suspended Particulates. EPA-600/4-78-047, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, 1978.



## APPENDIX B

### ESTABLISHING RELATIONSHIP OF ALTERNATIVE SAMPLING METHODS TO THE REFERENCE METHOD

#### 1.0 OCCASIONS WHEN RELATIONSHIP MUST BE ESTABLISHED

Whenever a method other than staggered PM<sub>10</sub> sampling or short time interval PM<sub>10</sub> sampling is to be used for episode monitoring, a specific site relationship with the reference method must be established and documented.

The advantage of using the staggered sampling or short time interval sampling methods is that these methods use the principle of the reference method. Consequently, in most cases, a specific site relationship need not be determined, thus reducing the testing time, testing cost, and the need perhaps for skilled personnel or expensive equipment.

The advantage of other methods over the two methods suggested above may be the advantage of automation, which could minimize the loss of time between air samples and important strategy decisions.

Requirements (see Table B-1) that must be satisfied to determine whether a method can be designated as equivalent to a reference method are found in Subpart C of 40 CFR Part 53. In addition, a candidate method must exhibit performance better than, or equal to, the requirement stated in Subpart D of 40 CFR Part 53. These criteria define what good comparable performance is for a monitoring method. A careful review of the full text of 40 CFR Part 53 should be made before testing for comparability of two methods in order to ensure that the most current rules are being applied. However, failure of a method to meet the specifications for comparability to

TABLE B-1. TEST SPECIFICATIONS FOR PM<sub>10</sub> METHODS

Acceptable concentration range, ug/m <sup>3</sup>	30 to 500
Minimum number of test sites	2
Number of candidate method sampler per site	3
Number of reference method samplers per site	3
Minimum number of 24-hour samples per sampler per site	15
Minimum number of acceptable sample sets per site	10
Precision of replicate reference method measurements	5 ug/m <sup>3</sup> or 7 percent
Slope of regression relationship	1 ± 0.1
Intercept of regression relationship, ug/m <sup>3</sup>	0 ± 5
Correlation of reference method and candidate method measurements	> 0.97



a reference method does not render the data from the candidate method useless. The procedure described below may be used to determine the correlation of the candidate method with a reference method and consequently allow those data to be assessed with respect to applicability to episode monitoring.

The remainder of this Appendix\* describes the procedures that should be followed to collect test data and to calculate, display, and assess a specific site relationship between a candidate method and the reference method.

## 2.0 TEST CONDITIONS FOR TAKING MEASUREMENTS

The reference method uses the filtration method described in Appendix A. The procedures described in Appendix A should be followed when sampling is done using the reference method. Sampling using alternate methods (candidate methods) for which the specific site relationship is to be established should be conducted according to the applicable manuals (e.g., manuals produced by instrument vendors that produce the instrument to be tested.

At least 10 ambient air measurements should be made simultaneously by the candidate and the reference method. The air samples should be taken simultaneously in the same area (i.e., within 2-3 meters of each other) without interference between samples or instruments. It is preferable to

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\* It is important to note that much of the text included in the remainder of this chapter follows very closely the text provided in an EPA document (EPA 450/4-79-007) referenced previously.

take all measurements during a single season, because site-specific relationships may vary with season. If more than one season is covered by the sample period, then 10 or more measurements per season should be made and results analyzed on a season-specific basis. The definition of a season is left to the discretion of those determining a site-specific relationship. In most areas of the contiguous United States, December through February is considered the winter season, with subsequent 3-month groupings comprising the remaining three seasons.

These measurements should be made on ambient air containing PM<sub>10</sub> concentrations in the range that the candidate method will be subjected to during an episode. To accomplish this, the measurements could initially be performed in nonepisodic (normal) atmospheric conditions to establish the relationship, but resumed during an episode to determine if the established relationship changes significantly. The relationship may be a function of the pollutant source, such as coal combustion, dust storms, or fuel use. If such is the case, then the relationship should be established under different source strengths.

If the candidate method has a shorter measuring time interval than the reference method, a sufficient number of sequential interval measurements should be made to equal the time period of the reference method (24 hours). The PM<sub>10</sub> concentration as determined by the reference method and the PM<sub>10</sub> concentration determined by the candidate method (or the mean of sequential determinations by the candidate method) are considered a "test pair."

All records, test data, procedural description and details, and other documentation obtained from (or pertinent to) tests made for the purpose of testing a candidate method should be identified, dated, and signed

by the tester. Test data are to be compiled and forwarded to the U.S. EPA Regional Office for approval.

### 3.0 METHODS FOR CALCULATING AND DISPLAYING THE RELATIONSHIP

The test pairs are used to estimate the functional relationship between the candidate and the reference methods. For a full season of 24-hour measurements taken every sixth day, 15 or 16 test pairs would be available in the absence of missing data. Hypothetical data (16 pairs) that are used to illustrate appropriate analytical methods appear in Table B-2. The method suggested for estimating a functional relationship between the candidate method (X) and the reference method (Y) is linear regression. Figure B-1 shows all calculations required to produce regression estimates and associated outputs from the inputs in Table B-2. The method suggested for displaying a relationship between values from the two methods is a scattergram, as illustrated in Figure B-2. The latter figure also includes the estimated regression line.

The essential outputs from the regression procedure are the estimated slope (Step 12 in Figure B-1), intercept (Step 13), and correlation coefficient (Step 14). The slope and intercept are required in order to make subsequent predictions based on the regression estimates (Step 15). The correlation coefficient is useful in assessing the strength of the association between values from the two methods. The residual mean square (Step 11) and sum of squared deviations about  $\bar{X}$  (Step 6) are necessary if one wishes to construct confidence intervals around predicted reference method values (Step 16). The value of  $t$ , used for a 95 percent confidence interval, varies with the number of test pairs. The appropriate number can be found in a table of  $t$ -values, which appears in most statistical texts.

TABLE B-2. SIMULATED DATA FOR CANDIDATE AND REFERENCE METHODS

X = PM-10 μg/m <sup>3</sup> Response measured by candidate method	Y = PM-10 Response measured by reference method
357	459
392	419
311	375
281	334
240	310
287	305
259	309
233	319
231	304
237	273
209	204
161	245
199	209
152	189
115	137
112	114

X denotes Candidate Method Response, Y denotes Reference Method Response  
( $\mu\text{g}/\text{m}^3$ )

a)  $\Sigma X = \text{Sum of } X$   
 $= 3776$

d)  $\Sigma Y = \text{Sum of } Y$   
 $= 4505$

b)  $\bar{X} = \Sigma X/n = \text{Average of } X$   
 $= 236$

e)  $\bar{Y} = \Sigma y/n = \text{Average of } Y$   
 $= 281.5625$

c)  $n = \text{Number of test pairs}$   
 $= 16$

Step (1):  $\Sigma XY = \text{Sum of } X \text{ times } Y$   
 $= 1,170,731$

Step (2):  $(\Sigma X)(\Sigma Y)/n$   
 $= 1,063,180$

Step (3):  $S_{xy} = \Sigma (X - \bar{X})(Y - \bar{Y})$  or  $\Sigma XY - (\Sigma X)(\Sigma Y)/n$   
Step (1) - Step (2)  
 $= 107,551$

Step (4):  $\Sigma X^2 = \text{Sum of each } X \text{ squared}$   
 $= 985,740$

Step (5):  $(\Sigma X)^2/n = a^2/c$   
 $= 891,136$

Step (6):  $S_{xx} = \Sigma (X - \bar{X})^2 = \text{Step (4)} - \text{Step (5)}$   
 $= 94,604$

Step (7):  $\Sigma Y^2 = \text{Sum of each } Y \text{ squared}$   
 $= 1,404,543$

Figure B-1. Basic worksheet showing the calculation steps.

Step (8):  $(\sum Y)^2/n = d^2/c$   
 $= 1,268,439$

Step (9):  $S_{yy} = \sum(Y - \bar{Y})^2 = \text{Step (7)} - \text{Step (8)}$   
 $= 136,104$

Step (10):  $\sum(\hat{Y} - Y)^2 = \text{Residual sum of squares (sum of squared differences between predicted and actual y values)}$   
 $= \sum(Y - \bar{Y})^2 - [(\sum(X - \bar{X})(Y - \bar{Y}))^2 / \sum(X - \bar{X})^2]$   
 $= \text{Step (9)} - [\text{Step (3)}]^2 / \text{Step (6)}$   
 $= 136,104 - (107,551^2 / 94,604)$   
 $= 13,834$

Step (11):  $S^2 = [\sum(\hat{Y} - Y)^2] / (n - 2) = \text{Residual mean square}$   
 $= \text{Step (10)} / (c - 2)$   
 $= 13,834 / 14 = 988$

Step (12):  $Z = S_{xy} / S_{xx} = \text{Slope of the regression curve}$   
 $= \text{Step (3)} / \text{Step (6)}$   
 $= 107,551 / 136,104 = 1.137$

Step (13):  $I = \bar{Y} - Z \bar{X} = Y \text{ intercept}$   
 $= e - \text{Step (12)b}$   
 $= 281.5625 - 1.137(236) = 13.23$

Step (14):  $r = \text{Correlation coefficient}$   
 $= S_{xy} / \sqrt{S_{xx}} \sqrt{S_{yy}}$   
 $= \text{Step (3)} / [\text{Step (6)}]^{1/2} [\text{Step (9)}]^{1/2}$   
 $= 107,551 / [136,104]^{1/2} [94,604]^{1/2}$   
 $= 0.948$

Figure B-1. (Continued)

Step (15): Prediction of Reference Method Value from Candidate Method Value

(a) Equation of regression line

$$Y = I + ZX$$

$$Y = 13.23 + 1.137 X$$

(b) Sample prediction

$$\text{Let } X_0 = 240$$

$$Y_0 = 13.23 + 1.137(240)$$

$$= 286.1$$

Step (16): 95 Percent Confidence Interval for Predicted Value ( $Y_0$ )

(a) Equation for interval

$$\text{Interval} = Y_0 \pm t_{n-2, 0.05} (S \sqrt{1 + 1/n + (X_0 - \bar{X})^2 / \sum (X - \bar{X})^2})$$

(b) Sample interval

$$\text{Let } X_0 = 240 \text{ and } Y_0 = 286.1, \text{ as in Step (15)}$$

$$\text{Interval} = 286.1 \pm 2.145 [\text{Step (11)}]^{1/2}$$

$$\times \sqrt{1 + 1/16 + (240-236)^2 / \text{Step (6)}}$$

$$= 286.1 \pm 2.145 (31.43) \sqrt{1 + 1/16 + (240-236)^2 / 94604}$$

$$= 286.1 \pm 2.145 (31.43) \sqrt{1.06267}$$

$$= 286.1 \pm 69.5$$

$$= (216.6, 355.6)$$

Figure B-1. (Concluded)

Advanced slide-rule calculators with statistical capability can be used to quickly obtain estimates of the slope, intercept, and correlation coefficient. With such a calculator, one needs only to input the test pairs. The estimates are retrievable by pushing specified keys on the calculator. With some algebraic manipulation, the residual mean square and sum of squared deviations can be derived from intermediate outputs, which are retrievable from selected memory areas within the calculator.

#### 4.0 METHODS FOR ASSESSING THE RELATIONSHIP

The regression procedure illustrated in Figure B-1 should be used only if the relationship between candidate and reference method values appears to be reasonably linear over the range of interest. A visual assessment of the degree of linearity can be made upon the basis of the scattergram (Figure B-2).

In cases where the relationship does not appear to be linear over the entire range of interest, other techniques for relating the two methods may be used. For example, some agencies have found that a piece-wise linear function is superior to a single linear function. Tests of significance are not as straightforward as for the linear case and require care in interpretation. Often, it is possible to linearize a nonlinear relationship by transformation of variables (e.g.,  $\sqrt{X}$ ,  $\log X$ , etc.). In such cases, the procedures outlined in the previous section of this Appendix may be applied to the transformed variables. In some rare cases, it may be necessary to use nonlinear regression techniques to properly fit the measured data.

The visual assessment of linearity should precede all calculations. Once a reasonable approximation to linearity has been achieved in the original or transformed data, the calculations shown in Figure B-1 can be



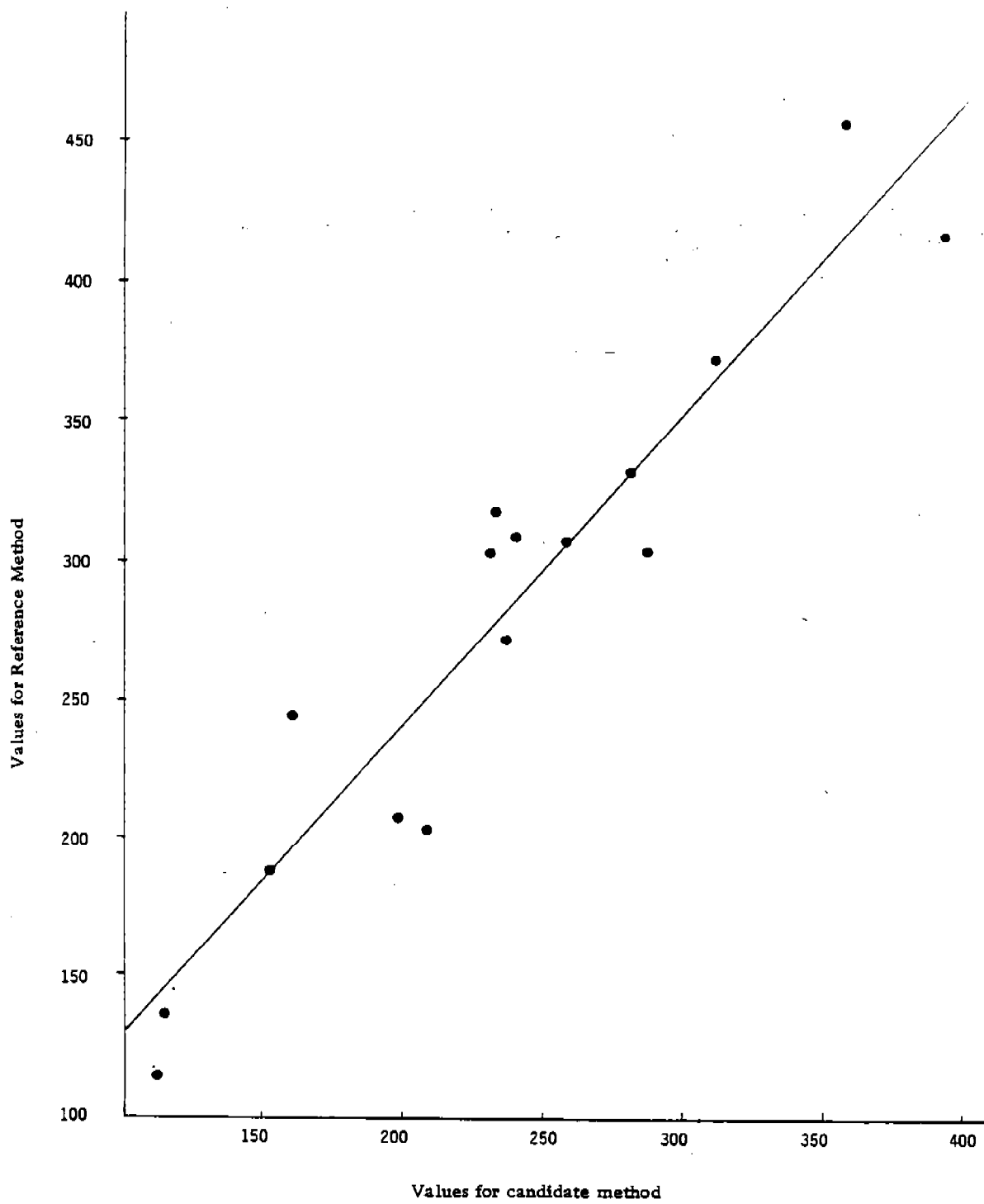


Figure B-2. Graph of relationship between candidate and reference method values.

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performed. The resultant regression equation can be used to draw the regression line through the data, as in Figure B-2. This line can be drawn by predicting Y values from X values at low and high extremes, plotting the resultant (X,Y) pairs, and connecting these plotted points. Any apparently nonrandom pattern of residuals about the regression line should then be readily discernible.

The strength of the association between the candidate and reference method values can be discerned by examining the correlation coefficient. In the case of 16 pairs, a correlation coefficient of 0.5 or greater is statistically significant at the 5 percent level. A coefficient of this magnitude, however, is of limited practical significance. The square of the correlation coefficient is a measure of the proportion of the variation in the reference method values explained by regression on the candidate method values. Thus, a correlation coefficient of 0.5 means that only 25 percent of the variation in reference method values is explained. A correlation coefficient of 0.7 means that approximately 50 percent of the variation is explained. Consequently, agencies are not advised to use a candidate method whenever the coefficient or correlation is less than 0.7. A more stringent cutoff level for candidate method acceptability would be a correlation coefficient of 0.85, which means that nearly 75 percent of the variation is explained.