United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/4-82-055 Dec. 1982

EPA

Test Methods

Technical Additions to Methods for Chemical Analysis of Water and Wastes

Notice

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Foreword

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

The preservation and holding times table and the six methods herein have been added to *Methods for Chemical Analysis of Water and Wastes*, EPA 600/4-79-020, as of the second printing, in an effort to provide updated analytical information to laboratories complying with the Safe Drinking Water Act, the National Pollutant Discharge Elimination System, Section 304(h) of the Clean Water Act, and the Ambient Monitoring Requirements of Sections 106 and 208 of Public Law 92-500.

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Table 1. *Recommendation for Sampling and Preservation of Samples According to Measurement*[1]

Measurement	Vol. Req. (mL)	Container[2]	Preservative[3,4]	Holding Time[5]
100 Physical Properties				
Color	50	P,G	Cool, 4°C	48 Hrs.
Conductance	100	P,G	Cool, 4°C	28 Days
Hardness	100	P,G	HNO_3 to pH<2	6 Mos.
Odor	200	G only	Cool, 4°C	24 Hrs.
pH	25	P,G	None Req.	Analyze Immediately
Residue				
Filterable	100	P,G	Cool, 4°C	7 Days
Non-Filterable	100	P,G	Cool, 4°C	7 Days
Total	100	P,G	Cool, 4°C	7 Days
Volatile	100	P,G	Cool, 4°C	7 Days
Settleable Matter	1000	P,G	Cool, 4°C	48 Hrs.
Temperature	1000	P,G	None Req.	Analyze Immediately
Turbidity	100	P,G	Cool, 4°C	48 Hrs.
200 Metals				
Dissolved	200	P,G	Filter on site HNO_3 to pH <2	6 Mos.[8]
Suspended	200		Filter on site	6 Mos.
Total	100	P,G	HNO_3 to pH <2	6 Mos.
Chromium^{+6}	200	P,G	Cool, 4°C	24 Hrs.
Mercury				
Dissolved	100	P,G	Filter HNO_3 to pH <2	28 Days
Total	100	P,G	HNO_3 to pH <2	28 Days
300 Inorganics, Non-Metallics				
Acidity	100	P,G	Cool, 4°C	14 Days
Alkalinity	100	P,G	Cool, 4°C	14 Days
Bromide	100	P,G	None Req.	28 Days
Chloride	50	P,G	None Req.	28 Days
Chlorine	200	P,G	None Req.	Analyze Immediately
Cyanides	500	P,G	Cool, 4°C NaOH to pH >12 0.6g ascorbic acid[6]	14 Days[7]
Fluoride	300	P,G	None Req.	28 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool, 4°C /H_2SO_4 to pH <2	28 Days
Kjeldahl, Total	500	P,G	Cool, 4°C H_2SO_4 to pH <2	28 Days
Nitrate plus Nitrite	100	P,G	Cool, 4°C H_2SO_4 to pH <2	28 Days
Nitrate[9]	100	P,G	Cool, 4°C	48 Hrs.
Nitrite	50	P,G	Cool, 4°C	48 Hrs.
Dissolved Oxygen				
Probe	300	G bottle and top	None Req.	Analyze Immediately
Winkler	300	G bottle and top	Fix on site and store in dark	8 Hours
Phosphorus				
Ortho-phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	48 Hrs.
Hydrolyzable	50	P,G	Cool, 4°C H_2SO_4 to pH <2	28 Days
Total	50	P,G	Cool, 4°C	28 Days

			H_2SO_4 to pH <2	
Total, Dissolved	50	P,G	Filter on site Cool, 4°C H_2SO_4 to pH <2	24 Hrs.
Silica	50	P only	Cool, 4°C	28 Days
Sulfate	50	P,G	Cool, 4°C	28 Days
Sulfide	500	P,G	Cool, 4°C add 2 mL zinc acetate plus NaOH to pH >9	7 Days
Sulfite	50	P,G	None Req.	Analyze Immediately
400 Organics				
BOD	1000	P,G	Cool, 4°C	48 Hrs.
COD	50	P,G	Cool, 4°C H_2SO_4 tp pH <2	28 Days
Oil & Grease	1000	G only	Cool, 4°C H_2SO_4 to pH <2	28 Days
Organic carbon	25	P,G	Cool, 4°C HCl or H_2SO_4 to pH <2	28 Days
Phenolics	500	G only	Cool, 4°C H_2SO_4 to pH <2	28 Days
MBAS	250	P,G	Cool, 4°C	48 Hrs.
NTA	50	P,G	Cool, 4°C	24 Hrs.

[1] More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72-82 (1976) Method D-3370.

[2] Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.

[3] Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting are completed.

[4] When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table 1, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[5] Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administrator. Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.

[6] Should only be used in the presence of residual chlorine.

[7] Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

[8] Samples should be filtered immediately on-site adding preservative for dissolved metals.

[9] For samples from non-chlorinated drinking water suplies conc. H_2SO_4 should be added to lower sample pH to less than 2. The sample should be analyzed before 14 days.

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Test Method

pH, Continuous Monitoring (Electrometric)—Method 150.2

1. Scope and Application

1.1 This method is applicable to the continuous pH measurement of drinking, surface, and saline waters, domestic and industrial waste waters.

2. Summary of Method

2.1 The pH of a sample is determined electrometrically using a glass electrode with a reference electrode or a single combination electrode.

3. Sample Handling and Preservation

3.1 The composition of the water or waste contacting the measuring electrode system must be representative of the total flow from the water body.

4. Interferences

4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.

4.3 Manually inspect the conditions of the electrodes every 30 days for coating by oily materials or buildup of lime. If oil and grease and/or scale buildup are not present, this time interval may be extended.

4.3.1 Coatings of oil, grease and very fine solids can impair electrode response. These can usually be removed by gentle wiping and detergent washing. The use of flow-through electrode housings which provide higher flow velocity helps to prevent the coating action.

4.3.2 Heavy particulate matter such as lime accumulation can be removed by careful scrubbing or immersion in dilute (1+9) hydrochloric acid. Continuous monitoring under these conditions benefits from ultrasonic or other in-line continuous cleaning methods.

4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. For best results, meters having automatic temperature compensation should be calibrated with solutions within 5°C of the temperature of the stream to be measured. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.

5. Apparatus

5.1 pH Monitor - A wide variety of instruments are commercially available with various specifications and optional equipment. For unattended use, the monitor should be equipped with automatic or fixed

temperature compensation and with a recorder or alarm function.

5.2 Glass electrode - with shielded cable between electrode and monitor unless preamplification is used.

5.3 Reference electrode - a reference electrode with a constant potential and with either a visible electrolyte or viscous gel fill.
NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

5.4 Temperature sensor - for automatic compensator covering general ambient temperature range.

5.5 Electrode mounting - to hold electrodes; may be flow through (for small flows), pipe mounted or immersion.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is required.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, which have been validated by comparison to NBS standards, is recommended for routine operation. These buffers may be retained for at least six months if kept stoppered.

7. Calibration

7.1 Immersion type electrodes - easily removed from mounting.

7.1.1 The electrode should be calibrated at a minimum of two points that bracket the expected pH of the water/waste and are approximately three pH units or more apart.

7.1.2 Repeat calibration adjustments on successive portions of the two buffer solutions until readings are within ±0.05 pH units of the buffer value. If calibration problems occur, see 4.3.

7.1.3 Because of the wide variety of instruments available, no detailed operating instructions are provided. Instead, the analyst should refer to the particular manufacturer's instructions.

7.1.4 Calibration against two buffers should be carried out at least daily. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data supports a longer period between calibration.

7.2 Immersion type electrodes - not easily removed from mounting.

7.2.1 Collect a grab sample of the flowing material from a point as close to the electrode as possible. Measure the pH of this grab sample as quickly as possible with a laboratory - type pH meter. Adjust the calibration control of the continuous monitor to the reading obtained.

7.2.2 The temperature and condition of the grab sample must remain constant until its pH has been measured by the laboratory pH meter. The temperature of the sample should be measured and the temperature compensator of the laboratory pH meter adjusted.

7.2.3 The laboratory - type pH meter should be calibrated prior to use against two buffers as outlined in 7.1.

7.2.4 The continuous pH monitoring system should be initially calibrated against two buffers as outlined in 7.1 before being placed into service. Recalibration (every 30 days) at two points is recommended if at all possible to ensure the measuring electrode is in working order. If this is not possible, the use of electrode testing features for a broken or malfunctioning electrode should be considered when purchasing the equipment.

7.2.5 The indirect calibration should be carried out at least once a day. If the pH of the fluid being measured fluctuates considerably, the calibration should be carried out more often. Calibration frequencies may be relaxed if historical data support a longer period between calibration.

7.2.6 If the electrode can be removed from the system, but with difficulty, it should be directly calibrated as in 7.1 at least once a month.

7.3 Flow-through type electrode - easily removed from its mounting.

7.3.1 Calibrate using buffers as in 7.1. The buffers to be used may be the process stream itself as one buffer, and as a second buffer after adjustment of pH by addition of an acid or base. This will provide the larger volumes necessary to calibrate this type electrode.

7.3.2 Since the velocity of sample flow-through a flow through electrode can produce an offset error in pH reading, the user must have data on hand to show that the offset is known and compensation has been accomplished.

7.4 Flow-through type electrode - not easily removed from its mounting.

7.4.1 Calibrate as in 7.2.

7.4.2 Quality control data must be on hand to show the user is aware of possible sample flow velocity effects.

8. Procedure

8.1 Calibrate the monitor and electrode system as outlined in Section 7.

8.2 Follow the manufacturer's recommendation for operation and installation of the system.

8.3 In wastewaters, the electrode may require periodic cleaning. After manual cleaning, the electrode should be calibrated as in 7.1 or 7.2 before returning to service.

8.4 The electrode must be placed so that the water or waste flowing past the electrode is representative of the system.

9. Calculations

9.1 pH meters read directly in pH units. Reports pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Because of the wide variability of equipment and conditions and the changeable character of the pH of many process waters and wastes, the precision of this method is probably less than that of Method 150.1; however, a precision of 0.1 pH unit

[1]National Bureau of Standards Special Publication 260.

should be attainable in the range of pH 6.0 to 8.0. Accuracy data for continuous monitoring equipment are not available at this time.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water" Standard 1293-78, Method D, p. 226 (1981).

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Test Method

Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes—Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in *drinking water, surface water,* domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interference are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, *appropriate steps must be taken to* correct for potential interference effects. (See 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and *typical estimated instrumental* detection limits using conventional pneumatic nebulization. Actual working detection limits are sample *dependent and as the sample matrix* varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are *monitored by photomultiplier tubes.* The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. *A background correction technique is* required to compensate for variable background contribution to the

determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 Dissolved — Those elements which will pass through a 0.45 μm membrane filter.

3.2 Suspended — Those elements which are retained by a 0.45 μm membrane filter.

3.3 Total — The concentration determined on an unfiltered sample following vigorous digestion (9.3), or the sum of the dissolved plus suspended concentrations. (9.1 plus 9.2.)

3.4 Total recoverable — The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (9.4).

3.5 Instrumental detection limit — The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 Sensitivity — The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 Instrument check standard — A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 Interference check sample — A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2)

3.9 Quality control sample — A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 Calibration standards — a series of know standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 Linear dynamic range — The concentration range over which the analytical curve remains linear.

3.12 Reagent blank — A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 Calibration blank — A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 7.5.1)

3.14 Method of standard addition — The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1)

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (14.7, 14.8 and 14.9) for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

The interference information, which was collected at the Ames Laboratory,[1] is expressed at analyte concentration eqivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the

[1]Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011

analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aersol flow-rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 Chemical Interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

5.2.1 Serial dilution—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 % of the original determination (or within some acceptable control limit (14.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

5.2.2 Spike addition—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect. *Caution:* The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended. (See 5.2.3)

5.2.3 Comparison with alternate method of analysis—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

5.2.4 Wavelength scanning of analyte line region—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

6.1.1 Computer controlled atomic emission spectrometer with background correction.

6.1.2 Radiofrequency generator.

6.1.3 Argon gas supply, welding grade or better.

6.2 Operating conditions — Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 Acetic acid, conc. (sp gr 1.06).

7.1.2 Hydrochloric acid, conc. (sp gr 1.19).

7.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distrilled water and dilute to 1 liter.

7.1.4 Nitric acid, conc. (sp gr 1.41).

7.1.5 Nitric acid,(1+1): Add 500 mL conc. HNO_3 (sp. gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 *Dionized, distilled water:* Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105°C unless otherwise specified.
(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:

7.3.1 Aluminum solution, stock, 1 mL = 100 μg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.2 Antimony solution stock, 1 mL = 100 μg Sb: Dissolve 0.2669 g K(SbO) $C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.3 Arsenic solution, stock, 1 mL = 100 μg As: Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.4 Barium solution, stock, 1 mL = 100 μg Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.5 Beryllium solution, stock, 1 mL = 100 μg Be: *Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4\ 4H_2O$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.6 Boron solution, stock, 1 mL = 100 μg B: *Do not dry.* Dissolve 0.5716 g anhydrous H_3BO_3 in deionized distilled water dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 Cadmium solution, stock, 1 mL = 100 μg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.8 Calcium solution, stock, 1 mL = 100 μg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.9 Chromium solution, stock, 1 mL = 100 μg Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.10 Cobalt solution, stock, 1 mL = 100 μg Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.11 Copper solution, stock, 1 mL = 100 μg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.12 Iron solution, stock, 1 mL = 100 μg Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.13 Lead solution, stock, 1 mL = 100 μg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.14 Magnesium solution, stock, 1 mL = 100 μg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.15 Manganese solution, stock, 1 mL = 100 μg Mn: Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1,000 mL with deionized, distilled water.

7.3.16 Molybdenum solution, stock, 1 mL = 100 μg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

7.3.17 Nickel solution, stock, 1 mL = 100 μg Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1,000 mL with deionized, distilled water.

7.3.18 Potassium solution, stock, 1 mL = 100 μg K: Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water dilute to 1,000 mL.

7.3.19 Selenium solution, stock, 1 mL = 100 μg Se: *Do not dry.* Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

7.3.20 Silica solution, stock, 1 mL = 100 μg SiO_2: *Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.21 Silver solution, stock, 1 mL = 100 μg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc. HNO_3. Dilute to 1,000 mL with deionized, distilled water.

7.3.22 Sodium solution, stock, 1 mL = 100 μg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.23 Thallium solution, stock, 1 mL = 100 μg Tl: Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.24 Vanadium solution, stock, 1 mL = 100 μg V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.25 Zinc solution, stock, 1 mL = 100 μg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.4 *Mixed calibration standard solutions*—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5) Add 2 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

7.4.1 Mixed standard solution I—Manganese, beryllium, cadmium, lead, and zinc.

7.4.2 Mixed standard solution II—Barium, copper, iron, vanadium, and cobalt.

7.4.3 Mixed standard solution III—Molybdenum, silica, arsenic, and selenium.

7.4.4 Mixed standard solution IV—Calcium, sodium, potassium, aluminum, chromium and nickel.

7.4.5 Mixed standard solution V— Antimony, boron, magnesium, silver, and thallium.

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 The reagent blank must concontain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8) and a quality control sample (3.9) are also required for the analyses.

7.6.1 The *instrument check standard* is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 12.1.1)

7.6.2 The *interference check sample* is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest by known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 μg/L or 5 times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 12.1.2)

7.6.3 The *quality control sample* should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 12.1.3)

8. Sample handling an preservation

8.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polyproplyene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See Notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chomic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

8.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferable at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 9.3.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc. HNO_3. Cover the

beaker with a watch glass and heat gently. The wam acid will soon dissolve the membrane.

Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See Note 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

NOTE 4: In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 mL of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total."

NOTE 5: If low determinations of boron are critical, quartz glassware should be use.

NOTE 6: If the sample analysis solution has a different acid concentration from that given in 9.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

10. Procedure

10.1 Set up instrument with proper operating parameters established in 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7: For boron concentrations greater than 500 $\mu g/L$ extended flush times of 1 to 2 min. may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than $\pm$ 5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See Note 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 samples.

10.6 If it has been found that method of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (14.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_X = \frac{S_B V_S c_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and c_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus c_S is much greater than c_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

11. Calculation

11.1 Reagent blanks (7.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures.

12. Quality Control (Instrumental)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

12.1.1 Analyze an appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ±5% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within the established control limits of two standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors analyze the interference check sample (7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.3 A quality control sample (7.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be anlayzed every week thereafter to monitor their stability. If the results are not within ±5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

Precision and Accuracy

13.1 In an EPA round robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

References

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Table 1. *Recommended Wavelengths [1] and Estimated Instrumental Detection Limits*

Element	Wavelength, nm	Estimated detection limit, µg/L[2]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see[3]
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[1] *The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1.).*

[2] *The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines, "EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.*

[3] *Highly dependent on operating conditions and plasma position.*

Table 2. *Analyte Concentration Equivalents (mg/L) Arising From Interferents at the 100 mg/L Level*

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	—	—	—	—	—	—	0.21	—	—	1.4
Antimony	206.833	0.47	—	2.9	—	0.08	—	—	—	.25	0.45
Arsenic	193.696	1.3	—	0.44	—	—	—	—	—	—	1.1
Barium	455.403	—	—	—	—	—	—	—	—	—	—
Beryllium	313.042	—	—	—	—	—	—	—	—	0.04	0.05
Boron	249.773	0.04	—	—	—	0.32	—	—	—	—	—
Cadmium	226.502	—	—	—	—	0.03	—	—	0.02	—	—
Calcium	317.933	—	—	0.08	—	0.01	0.01	0.04	—	0.03	0.03
Chromium	267.716	—	—	—	—	0.003	—	0.04	—	—	0.04
Cobalt	228.616	—	—	0.03	—	0.005	—	—	0.03	0.15	—
Copper	324.754	—	—	—	—	0.003	—	—	—	0.05	0.02
Iron	259.940	—	—	—	—	—	—	0.12	—	—	—
Lead	220.353	0.17	—	—	—	—	—	—	—	—	—
Magnesium	279.079	—	0.02	0.11	—	0.13	—	0.25	—	0.07	0.12
Manganese	257.610	0.005	—	0.01	—	0.002	0.002	—	—	—	—
Molybdenum	202.030	0.05	—	—	—	0.03	—	—	—	—	—
Nickel	231.604	—	—	—	—	—	—	—	—	—	—
Selenium	196.026	0.23	—	—	—	0.09	—	—	—	—	—
Silicon	288.158	—	—	0.07	—	—	—	—	—	—	0.01
Sodium	588.995	—	—	—	—	—	—	—	—	0.08	—
Thallium	190.864	0.30	—	—	—	—	—	—	—	—	—
Vanadium	292.402	—	—	0.05	—	0.005	—	—	—	0.02	—
Zinc	213.856	—	—	—	0.14	—	—	—	0.29	—	—

Table 3. *Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2.*

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

Table 4. *ICP Precision and Accuracy Data*

Element	Sample # 1			Sample #2			Sample #3		
	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Chromium, Dissolved Hexavalent (Atomic Absorption, Furnace Technique)—Method 218.5

1. Scope and Application

1.1 This method covers the determination of dissolved hexavalent chromium (Cr^{6+}) in drinking and surface waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that potential interferring substances are taken into account. (See 4.1.)

1.2 The method may be used to analyze samples containing from 5 to 100 μg of Cr^{6+} per liter. The range of the method may be extended upward by dilution.

2. Summary of Method

2.1 The method is based on the separation of Cr^{6+} from the sample by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate is drawn off and the Cr^{6} precipitate resolubilized in nitric acid as trivalent chromium (Cr^{3+}) and quantified by furnace atomic absorption.

2.2 Hexavalent chromium may also be analyzed by the chelation/extraction technique (see Method 218.4 or the procedure described in 9.2 of the Atomic Absorption methods found in this manual).

3. Sample Handling and Preservation

3.1 For sample handling, cleaning glassware and the filtration procedure see part 4.1 of the Atomic Absorption Method section of this manual.

3.2 The sample must not be preserved by acidification, but instead transported and stored until time of analysis at 4°C.

3.3 Stability of Cr^{6+} in environmental samples is n ot completely understood at this time. The chemical nature of the sample matrix can have a definite affect on the chemistry of chromium. Therefore, the analysis should be carried out as soon as possible but no longer than 24 hours after collection.

4. Interferences

4.1 The possible interference from other elements which form stable chromates is not known at this time.

4.2 Samples with either sulfate or chloride concentrations above 1000 mg/liter should be diluted before analysis.

4.3 The potential reduction of Cr^{6+} from highly reductive substances increases as pH is lowered. When sulfites and sulfides are present the

sample aliquot taken for analysis should be neutralized and aerated before beginning.

5. Instrument Parameters (General)

5.1 Drying Time and Temp: 30 sec-125°C.

5.2 Ashing Time and Temp: 30 sec-1000°C.

5.3 Atomizing Time and Temp: 10 sec-2700°C.

5.4 Purge Gas Atmosphere: Argon

5.5 Wavelength: 357.9nm

5.6 Other operating parameters should be as specified by the particular instrument manufacturer.

6. Special Apparatus

6.1 Glassware

6.1.1 Filtering flask, heavy wall, 1 liter capacity

6.1.2 Centrifuge tubes, heavy duty, conical, graduated, glass stoppered, 10 mL capacity

6.1.3 Pasteur pipets, borosilicate glass, 5 ¾ inches.

6.2 Centrifuge: any centrifuge capable of reaching 2000 rpm and accepting the centrifuge tubes described in 6.1.2 may be used.

6.3 pH Meter: a wide variety of instruments are commercially available and suitable for this work.

6.4 Test Tube Mixer: any mixer capable of thorough vortex is acceptable.

7. Reagents

7.1 Lead Nitrate Solution: Dissolve 33.1 grams of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.2 Ammonium Sulfate Solution: Dissolve 2.7 grams of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL.

7.3 Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.

7.4 Nitric Acid, conc.: Distilled reagent grade or equivalent to spectrograde quality.

7.5 Acetic Acid, Glacial: ACS reagent grade.

7.5.1 Acetic Acid, 10% (v/v): Dilute 10 mL glacial acetic acid to 100 mL with deionized distilled water.

7.6 Ammonium Hydroxide, 10% (v/v): Dilute 10 mL conc ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with deionized distilled water.

7.7 Hydrogen Peroxide, 30%: ACS reagent grade.

7.8 Potassium Dichromate Standard Solution: Dissolve 2.8285 grams of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in deionized distilled water and dilute to 1 liter. 1 mL = 1 mg Cr (1000 mg/L)

7.9 Trivalent Chromium Working Stock Solution: To 50 mL of the potassium dichromate standard solution (7.8) add 1 mL of 30% H_2O_2 (7.7) and 1 mL conc. HNO_3 (7.4) and dilute to 100 mL with deionized distilled water 1 mL = 0.5 mg Cr^{3+}. Prepare fresh monthly or as needed.

8. Calibration

8.1 At the time of analysis prepare a blank and a series of at least four calibration standards from the Cr^{3+} working stock (7.9) that will adequately bracket the sample. The normal working range covers a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard 1 mL 30% H_2O_2 (7.7), 5 mL CONC HNO_3 (7.4), and 1 mL calcium nitrate solution (7.3) for each 100 mL of prepared solution before diluting to final volume. These calibration standard should be prepared fresh weekly or as needed.

8.2 The listed instrumental conditions (5.) and the stated calibration concentration range are for a Perkin-Elmer HGA-2100 based on the use of a 20μL injection, continous flow purge gas and non-pyrolytic graphite. The use of simultaneous background correction is required for both calibration and sample analysis.

9. Procedure

9.1 Transfer a 50 mL portion of the filtered sample to a 100mL Griffin beaker and adjust to pH 3.5±0.3 by adding 10% acetic acid dropwise. Record the volume of acid added and adjust the final result to account for the dilution.

Note: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to < 3, 10% NH_4OH (7.6) should be used to raise the pH to above 3.

9.2 Pipet a 10 mL aliquot of the adjusted sample into a centrifuge tube (6.1.2). Add 100μL of the lead nitrate solution (7.1), stopper the tube, mix the sample and allow to stand for 3 min

9.3 After the formation of lead chromate, retain the Cr^{3+} complex in solution by addition of 0.5 mL glacial acetic acid (7.5). Stopper and mix.

9.4 To provide adequate lead sulfate for coprecipitation add 100 mL ammonium sulfate solution (7.2), stopper and mix.

9.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2000 rpm in small increments over a period of 5 min. Centrifuge the sample at 2000 rpm for 10 min.

Note 2: The speed of the centrifuge must be increased slowly to insure complete coprecipitation.

9.6 After centrifuging remove the tube and draw off the supernate using the apparatus detailed in Figure 1. As the pasteur pipet is lowered into the tube the supernate is sucked into the filtering flask. With care the supernate can be withdrawn to within approximately 0.1 mL above the precipitate.

9.7 To the remaining precipitate add 0.5 mL conc HNO_3 (7.4), 100μL 30% H_2O_2 (7.7) and 100μL calcium nitrate solution (7.3). Stopper the tube and mix using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10mL, mix and analyze in the same manner as the calibration standard (8.2).

9.8 For the general furnace procedure and calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

10. Verification

10.1 For every sample matrix analyzed verification is necessary to determine that neither a reducing condition nor a chemical interference affecting precipitation is present. This

must be accomplished by analyzing a second 10mL aliquot of the pH adjusted filtrate (9.1) spiked with Cr^{6+} (7.8). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be of less than 30μg Cr^{6+}/L. To verify the absence of an interference the spike recovery should be between 85% and 115%.

10.2 If the addition of the spike extends the concentration beyond the range of the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

10.3 If the verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

11. Analytical Notes

11.1 Nitrogen should not be used as a purge gas because of possible CN band interference.

11.2 The use of pyrolytic graphite should be avoided when possible. Generally, pyrolytic graphite resulted in a more limited analytical working range and in some situations an enhancement effect.

11.3 Pipet tips have been reported to be a possible source of contamination. (See part 5.2.9 of the Atomic Absorption Methods section of this manual.)

11.4 The method of standard addition should not be required in as much as the Cr^{6+} has been separated from the original sample solution and redissolved in a uniform matrix having an absorption response coincident to the calibration curve.

11.5 Data to be entered into STORET (No. 01032) must be reported as μg/L.

12. Precision and Accuracy

12.1 In a single laboratory (EMSL) using a mixed industrial-domestic waste effluent containing 22 μg Cr^{6+}/L and spiked with a concentration of 50 μg Cr^{6+}/L the standard deviations were $\pm$ 1.0 and $\pm$ 2.7, respectively with a spike recovery of 94%.

12.2 Recoveries of a 40 μg Cr^{6+}/L spike in diluted tannery and plating waste effluents were 96% and 93%, respectively.

12.3 Using Cincinnati, Ohio tap water spiked at concentrations of 5,10, and 50 μg Cr^{6+}/L the standard deviations were $\pm$ 0.7, $\pm$0.6, and $\pm$0.6, respectively. Spike recovery at all three levels was 102%.

12.4 A 1000 μg Cr^{3+}/L standard solution analyzed by this method yielded a result of 8 μg Cr^{6+}/L with a relative standard deviation of 19%.

12.5 The data from 5 μg Cr^{6+}/L tap water spike was used to calculate method detection limit (MDL) with 99% confidence as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, *Environmental Science and Technology,* Vol. 15, Number 12, page 1426, December 1981. The calculated MDL for Cincinnati drinking water is 2.3 μg/L.

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Test Method

Sodium (Atomic Absorption, furnace technique)—Method 273.2

Optimum Concentration Range: 1-30 μg/L
Detection Limit: 0.2 μg/L
Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method."
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 250°C
3. Atomizing Time and Temp: 10 sec @ 2000°C.
4. Purge Gas atmosphere: Argon
5. Wavelength: 589.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" 9.3 of the Atomic Absorption method section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 μL injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Samples containing concentrations higher than those given in the optimum range should be analyzed by either the direct aspiration method (Method 273.1) or the flame photometric method (Std. Methods, 14th Edition, p. 250).
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see 5.2.1 of the Atomic Absorption method section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in 8.5 of the Atomic Absorption methos section of this manual.

6. Data to be entered into STORET must be reported as µg/L.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

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Test Method

Acidity (Titrimetric)—Method 305.2

1. Scope and Application

1.1 This method is applicable to rain, surface and other waters of pH less than 8.3.

1.2 This method is a measure of the concentration of strong and weak acids that react with hydroxyl ions. This includes the dissolved gases that are present.

1.3 The range of this method depends on the volume of sample titrated and upon the precision that the increments of titrant can be measured. If only 10 mL of sample is available for analysis, it is necessary to use a 50 μL syringe for dispensing the titrant in order to achieve a precision of less than 10 μeq/L.

2. Summary of Method

2.1 Samples are titrated with 0.02 N carbonate free NaOH solution. The end point is determined with a pH meter. Results are reported as microequivalents (μeq) per liter.

3. Sampling Handling and Storage

3.1 The sample container must be filled completely, sealed and stored at 4°C. Care must be taken to minimize exposure of the sample to the atmosphere. Open the sample container immediately before analysis.

3.2 Analysis should be performed as soon as possible after collection.

4. Comments

4.1 Samples with an initial pH between 4.3 and 8.3 are subject to error due to the loss or gain of dissolved gases during sampling, storage and analyses.

5. Apparatus

5.1 pH meter and electrode(s), see Method 150.1 or 150.2.

5.2 Micro buret or micro syrings.

5.3 Teflon or glass magnetic stirring bar.

5.4 Magnetic stirrer.

5.5 Beakers or flasks.

6. Reagents

6.1 Standard sodium hydroxide solution, 1 N: Dissolve 40g NaOH in 250 mL distilled water. Cool and dilute to 1 liter with CO_2 free distilled water. Store in a polyolefin bottle and fitted with a soda lime tube or tight cap to protect from atmospheric CO_2.

6.2 Standard sodium hydroxide titrant, 0.02 N: Dilute 20.0 mL of 1 N NaOH with CO_2-free distilled water to 1 liter. Store in rubber stoppered bottle. Protect from atmospheric CO_2 by using a soda lime tube. Standardize against an 0.02 N potassium acid phthalate solution prepared by dissolving 4.085 g of anhydrous $KHC_8H_4O_4$ in CO_2 free distilled water and diluted to 1:1.

7. Procedure

7.1 Pipet an appropriate aliquot of sample into beaker of flask containing a small teflon on glass stirring bar. Use extreme care to minimize the sample surface disturbance.

7.2 Immerse pH electrode(s) into sample and stir at a rate that does not cause sample surface disturbance.

7.3 Titrate with 0.02 N NaOH (6.2) to pH 8.3. Titration should be made as quickly as possible to prevent absorption of atmospheric CO_2. Record volume of titrant.

8. Calculation

8.1 **Acidity,** $\mu eq/L = \frac{mL_B}{mL_S} \times N_B \times 10^5$

$\mu eq/L$ = microequivalents per liter

mL_B = mL of NaOH titrant

mL_S = mL of sample

N_B = normality of titrant

9. Precision and Accuracy

9.1 Precision and accuracy data are not available.

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Test Method

Organic Carbon, Total (low level) (UV promoted, persulfate oxidation)—Method 415.2

1. Scope and Application

1.1 This method covers the determination of total organic carbon in drinking water and other waters subject to the limitations in 1.3 and 5.1.

1.2 This instrument is designed for a two-step operation to distinguish between purgeable and nonpurgeable organic carbon. These separate values are not pertinent to this method.

1.3 This method is applicable only to the carbonaceous matter which is either soluble or has a particle size of 0.2 mm or less.

1.4 The applicable range is from approximately 50 μg/L to 10 mg/L. Higher concentrations may be determined by sample dilution.

2. Summary of Method

A sample is combined with 1 mL of acidified persulfate reagent and placed in a sparger. The sample is purged with helium which transfers inorganic CO_2 and purgeable organics to a CO_2 scrubber. The CO_2 is removed with at least 99.9% efficiency with a 2.5-minute purge. The purgeable organics proceed through a reduction system where the gas stream is joined by hydrogen and passed over a nickel catalyst which converts the purgeable organic carbon to methane. The methane is measured by a flame ionization detector. The detector signal is integrated and displayed as the concentration of purgeable organic carbon.

The sample is then transferred to a quartz ultraviolet reaction coil where the nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent. The nonpurgeables are converted to CO_2 and transferred to a second sparger where a helium purge transfers the CO_2 to the reduction system and into the detector. The signal is integrated, added to the purgeable organic carbon value, and displayed as the concentration of total organic carbon.

3. Definitions

3.1. Total organic carbon measured by this procedure is the sum of the purgeable organic carbon and the nonpurgeable organic carbon as defined in 3.2 and 3.3.

3.2 Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO_2 scrubber. The definition is instrument-condition dependent.

3.3 Nonpurgeable organic carbon is defined as that which remains after removal of the purgeable organic carbon from the sample containing acidified persulfate reagent and which

is converted to CO_2 under the instrument conditions.

3.4 The system blank is the value obtained in 8.2 for an irradiated, recirculated reagent distilled water sample.

4. Sample Handling and Preservation

4.1 Sampling and storage of samples must be done in glass bottles. Caution: Do not leave any headspace in the sample bottle as this may contribute to loss of purgeable organics.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 When analysis cannot be performed within two hours from time of sampling, the sample should be acidified to pH 2 with H_2SO_4. Note: HCl should not be used because it is converted to chlorine during the analysis. This causes damage to the instrument.

5. Interferences

5.1 If a sample is homogenized to reduce the size of the particulate matter, the homogenizing may cause loss of purgeable organic carbon, thus yielding erroneously low results.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: A household blender or similar device that will reduce particles in the sample to less than 0.2 mm.

6.2 Apparatus for Total Organic Carbon: The essential components for the apparatus used in this method are: A sparge assembly, flow switching valves, a pyrolysis furnace, quartz ultraviolet reactor coil, reducing column, flame ionization detector, electrometer and integrator. This method is based on the Dohrmann Envirotech DC-54 Carbon Analyzer. Other instruments having similar performance characteristics may be used.

6.3 Sampling Devices: Any apparatus that will reliably transfer 10 mL of sample to the sparger. A 50 mL glass syringe is recommended when analyzing samples with easily purgeable organics so as to minimize losses.

7. Reagents

7.1 Reagent Distilled Water: Distilled water used in preparation of standards and for dilution of samples should be ultra-pure to reduce the magnitude of the blank. Carbon dioxide-free, double distilled water is recommended. The water should be distilled from permanganate or be obtained from a system involving distillation and carbon treatment. The reagent distilled water value must be compared to a system blank determined on a recirculated distilled water sample. The total organic carbon value of the reagent distilled water should be less than 60 μg/L. Purgeable organic carbon values of the reagent distilled water should be less than 4 μg/L.

7.2 Potassium hydrogen phthalate, stock solution, 500 mg carbon/liter: Dissolve 1.063 g of potassium hydrogen phthalate (Primary Standard Grade) in reagent distilled water (7.1) and dilute to 1 liter.

7.3 Potassium hydrogen phthalate (2 mg/L): Pipet 4 mL of potassium hydrogen phthalate stock solution (7.2) into a one liter volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.4 Potassium hydrogen phthalate (5 mg/L): Pipet 1 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.5 Potassium hydrogen phthalate (10 mg/L): Pipet 2 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.6 Acidified Persulfate Reagent: Place 100 mL of reagent distilled water (7.1) in a container. Add 5 g of potassium persulfate. Add 5 g (3 mL) of concentrated (85%) phosphoric acid.

7.7 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Place 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in a 100 mL volumetric flask. Dissolve with reagent distilled water (7.1) and dilute to the mark.

7.8 Carbonate-bicarbonate, standard solution 50 mg/L: Place 5 ml of the carbonate-bicarbonate stock solution in a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

8. Procedure

8.1 Allow at least 30 minutes warm-up time. Leave instrument console on continuously when in daily use, except for the ultraviolet light source, which should be turned off when not in use for more than a few hours.

8.2 Adjust all gas flows, temperatures and cycle times to manufacturer's specifications. Perform the "System Cleanup and Calibration" procedure in the manufacturer's specifications each day. Recirculate a sample of irradiated distilled water until two consecutive readings within 10% of each other are obtained. Record the last value for the system blank. This value is a function of the total instrument operation and should not vary significantly from previous runs. Reasons for significant changes in the value should be identified.

8.3 Check the effectiveness of the CO_2 scrubber by analyzing the carbonate-bicarbonate standard solution(7.8). Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of the solution. Transfer 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle. No response, or a very minor reading, should be obtained from this solution.

8.4 Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of reagent distilled water (7.1) blank, standards 7.3, 7.4, and 7.5 and the samples.

8.5 Calibrate the analyzer as follows:

8.5.1 Run the reagent distilled water (7.1) and 5.0 mg/L standard (7.4): Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle

Record the meter reading (see 9.1) of the final carbon value for each of the reagent distilled water (7.1) and the standard (7.4).

If the meter reading is more than 25% above or below the calculated value of standard 7.4, reanalyze the standard

and set the calibration within 25% (8.5.4), reanalyze the system blank, and then begin 8.5.1 again. If the meter reading (see 9.1) is within 25% of the calculated value, continue to next step. The calculated value is defined in 8.5.2.

8.5.2 Calculate the factor for the deviation of the instrument reading (see 9.1) for the standard (7.4) from the calculated value by:

$$\frac{\text{standard reading} - \text{calculated value}}{\text{calculated value}} = \text{FACTOR}$$

where the calculated value is that value obtained by using the weight of potassium hydrogen phthalate and does not include the carbon contributed by the reagent distilled water (7.1) with which it has been diluted.

8.5.3 Calculate the adjusted reading by:
calculated value + (RDW - (FACTOR X RDW)) = ADJUSTED READING.
where RDW = mean reagent distilled water (7.1) value.

8.5.4 Push in CALIBRATE button after READY light comes on and adjust the SPAN control to the ADJUSTED READING calculated in 8.5.3.

8.6 Analyze the standards 7.3 and 7.5 in order to check the linearity of the instrument at least once each day:

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the standards 7.3 and 7.5.

The range of concentration used for calibrating the instrument and checking the linearity of the instrument should be ascertained from a knowledge of the range of concentrations expected from the samples. Standards for lower ranges can be prepared by diluting standards 7.2, 7.3, and 7.4.

8.7 Analyze the samples. Transfer 10 mL of sample with reagent to the first sparger and start the analysis cycle.

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the samples.

9. Calculations

9.1 The values are read off the final digital readout in $\mu g/L$. The system blank reading obtained in 8.2 must be subtracted from all reagent distilled water, standard and sample readings.

10. Precision and Accuracy

10.1 In a single laboratory (MERL), using raw river water, centrifuged river water, drinking water, and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/L total organic carbon respectively, the standard deviations from ten replicates were ± 0.13, ± 0.03, ± 0.02, and ± 0.02 mg/L, respectively.

10.2 In a single laboratory (MERL), using potassium hydrogen phthalate in distilled water at concentrations of 5.0 and 1.0 mg/L total organic carbon, recoveries were 80% and 91%, respectively.

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* U.S. GOVERNMENT PRINTING OFFICE: 1983-659-095/0569