California Environmental Protection Agency

Air Resources Board

Method 425

Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources

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1 APPLICABILITY AND PRINCIPLES

1.1 Applicability

This method applies to the determination of hexavalent chromium (Cr6) and total chromium (Cr) emissions from stationary sources. Applicability has been demonstrated for the metal finishing and glass industries. Its applicability has not been demonstrated for sources with high particulate mass emission rates.

The ion chromatographic-colorimetric (IC-C) analytical procedure described is applicable to filter extracts and emission samples collected in impinger solutions of 0.1M sodium hydroxide solution. It is also applicable to samples in water or in the ammonium hydroxide/ammonium sulfate eluent solution described herein. Preconcentration of larger volumes of the sample on an anion guard column prior to injection to increase the sensitivity of the procedure cannot be recommended at this time due to the levels of chromate and interfering compounds found in the commonly available grades of sodium hydroxide and because of the tendency of sodium hydroxide to act as an internal eluent on the preconcentration column.

Any modification of this method shall be subject to approval by the Executive Officer. The term "Executive Officer", as used in this document, shall mean the Executive Officer of the Air Resources Board, or his or her authorized representative.

1.2 Sampling Principle

Particulate emissions are collected from the source in an alkaline medium by use of CARB Method 5, with modifications noted in this method.

1.3 Recovery Principle

The components of the collected sample are each divided into two equal portions with one portion of each component used for total chromium analysis and the other portion used for hexavalent chromium analysis.

1.4 Cr6 Ion Chromatographic-Colorimetric (IC-C) Analytical Principle

This procedure, as described, uses direct sample injection and post column derivatization with a 1,5 diphenylcarbazide colorimetric reagent and photometric detection at 540 nm. Hexavalent chromium is separated from other metallic anions as chromate by a high capacity anion separator column and a colored product having a wide absorption band centered at approximately 540 nm is formed by reaction with the colorimetric reagent. The colored reaction product is detected photometrically and quantitation as Cr6 is accomplished by linear regression of either peak area or peak height on the concentration of a series of Cr6 calibration standards.

1.5 Cr6 Manual-Colorimetric (M-C) Analytical Principle

For the hexavalent chromium analysis the collected sample component portions are extracted in an alkaline solution and analyzed by the diphenylcarbazide colorimetric method which requires 35mL of sample liquid per analysis.

1.6 Cr Graphite Furnace-Atomic Absorption (GF-AA) Analytical Principle

For the total chromium analysis the collected samples shall be prepared in order to convert organic forms of chromium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. Samples are then subjected to an acid digestion procedure. Following the appropriate dissolution and dilution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the chromium concentration.

2 DEFINITIONS

2.1 End User

For the purposes of this method, the regulating agency or its authorized representative shall be considered the end user if a determination of Cr and Cr6 emissions from a stationary source is required as part of a regulatory process. Otherwise the end user shall be the party who defrays the cost of performing this method. The pre-test protocol must identify the end user.

2.2 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). The tester shall ultimately be responsible for performance of this method whether directly or indirectly through co-ordination of the efforts of the sampling and analytical groups.

2.3 Source Target Concentration

This is the target concentration for hexavalent chromium (Cr6) specified by the end user of the test results. The target concentration shall be expressed in units of Cr6 mass per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/m^3 or $\mu g/m^3$).

2.4 Limit of Detection

The limit of detection (LOD) is a limit of the performance of the analytical procedures below which quantitative results must not be reported. The LOD is based on the absolute value of the x-intercept of the calibration plot for absorbance versus concentration adjusted by three times the standard deviation of the absorbance for a mid-point concentration.

2.5 Reporting Limit

The reporting limit (RL) is a limit of the performance of the entire test method below which quantitative mass analyses must not be reported for a given sample run. The RL is based on the minimum analyte mass that must be collected in the sampling train to allow detection by the laboratory according to the requirements of this method. Such mass is the product of the LOD and the liquid volume used to collect the analyte in the sampling train.

2.6 Source Reporting Limit

The source reporting limit (SRL) is a limit of the performance of the entire test method below which quantitative emission results must not be reported.

3 PRE-TEST PROTOCOL

3.1 Responsibilities of the End User and Tester

3.1.1 The End User

Before testing may begin, the end user of the test results must specify the source target concentration to be determined by this method using the guidelines of § 3.2.1.

The end user shall approve the pre-test protocol after reviewing the document and determining that the minimum requirements for the pre-test protocol (§ 3.2) have been met.

3.1.2 The Tester

The tester shall have primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the sampling and analytical groups.

The tester shall plan the test based on the information provided by the end user and the tester's calculations of target source testing parameters.

The tester shall be responsible for selection of an analyst qualified for use of the method. The tester shall make that decision based on information supplied by the analyst.

The tester shall obtain all relevant data that are required for pre-test calculations of sampling parameters. The tester shall develop and write a pre-test protocol before performing this method to help ensure satisfactory results.

The tester shall be responsible for ensuring that all sampling and analytical reporting requirements are met.

3.2 Pre-Test Protocol

The pre-test protocol should include the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

(1) source target concentration of Cr6 (§ 3.2.1),
(2) preliminary analytical data (§ 3.3) for Cr6, and
(3) planned sampling parameters (§ 3.5).

The protocol must demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. In addition, the pre-test protocol should include information on equipment, logistics, personnel and other resources necessary for an efficient and coordinated test.

At a minimum, the pre-test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be approved by the end user of the results and the tester.

The tester should not proceed with the performance of the remainder of this method unless the pre-test protocol is approved by the tester and the end user.

3.3 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

(1) Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

(2) Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

(3) Interests of the End User, the Tester, and the Stationary Source

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user may use emissions results from previous tests of the facility or from similar sources. This target concentration is necessary for the calculation of the target sampling parameters required by § 3.5.

3.4 Preliminary Calculations

3.4.1 Determining the Limit of Detection (LOD)

The "Analytical Calibration Procedure" of this test procedure which is appropriate for the target substance shall be used for the analytical calibration and the determination of the limit of detection (LOD) described below. Such analytical calibration shall be performed prior to

sampling by the same analytical personnel who perform the analytical calibration subsequent to sampling; this does not exclude the use of documentation for analytical calibration performed for prior tests.

(1) Plotting Absorbance versus Concentration

Plot absorbance as the dependent variable (y-axis) and concentration as the independent variable (x-axis).

(2) Determining the Standard Deviation at the Midpoint

Prepare a standard solution of the target substance with a concentration near the midpoint of the calibration curve.

Analyze four or more aliquots of this solution and plot the results.

Calculate the standard deviation, s_{mid}, of the absorbance.

(3) Calculating the X-Intercept and Slope

Using the least squares method, determine the x-intercept, a, and slope, n, of the line through the data.

Equation 425-1 shall be used to calculate the LOD.

$$LOD = |a| + \left(\frac{3s_{mid}}{n} \right) \qquad 425\text{-}1$$

Where:

LOD	=	limit of detection, ng/mL
$\|a\|$	=	absolute value of x-intercept, ng/mL
$3s_{mid}$	=	three times the standard deviation of the midpoint absorbance, absorbance units
n	=	slope of the calibration line, (absorbance units)/(ng/mL)

3.4.2 Determining the Reporting Limit (RL)

To obtain the lowest RL, assume that:

(1) all of the Cr6 in the gas sampled is recovered from the liquid of the probe rinse and the first impinger and

(2) the volume of the liquid of the probe rinse and the first impinger is 220 mL. Equation 425-2 shall be used to calculate the RL.

$$RL = LOD \times 220 \qquad 425\text{-}2$$

Where:

RL = analytical mass reporting limit, ng

LOD = limit of detection, ng/mL

220 = liquid volume of probe rinse and first impinger, mL

3.5 Sampling Runs, Time, and Volume

3.5.1 Sampling Runs

A test shall include at least three sampling runs in series and a blank sampling train.

3.5.2 Minimum Sample Volume (MSV)

This is the minimum sample volume that must be collected in the sampling train to provide sufficient Cr6 for analytical quantitation. The MSV must be based on the reporting limit and the source target concentration. The MSV will be adjusted, based on further practical limitations, to yield the planned sample volume (PSV) in subsequent sections.

Equation 425-3 shall be used to calculate the MSV.

$$MSV = RL \times \frac{1}{STC} \qquad 425\text{-}3$$

Where:

MSV = minimum sample volume, dscm

RL = analytical mass reporting limit, ng

STC = source target concentration, ng/dry standard cubic meters (dscm)

3.5.3 Minimum Sampling Time (MST)

This is the minimum time required to collect the minimum sample volume at the expected volumetric sampling rate. The tester should use an average volumetric sampling rate (VSR)

appropriate for the source to be tested. If the VSR cannot be achieved in the field, the sampling time shall be revised using the following equation to achieve the target MSV. The sampling time must be such that the emissions test is conducted during representative operating conditions of the source.

Equation 425-4 shall be used to calculate the MST.

$$MST = \frac{MSV}{VSR} \qquad 425\text{-}4$$

Where:

MST = minimum sampling time, hours

MSV = minimum sample volume, dscm

VSR = volumetric sampling rate, dscm/hour

3.5.4 Planned Sample Volume (PSV)

The planned sample volume (PSV) is the volume of emissions that must be sampled to collect for analysis a mass of Cr6 between the RL and the limit of linearity. The PSV is the primary sampling target whenever practically feasible. Calculate the PSV using the largest value for F that will give a practical sample volume.

Equations 425-5 and 425-6 shall be used to calculate the PSV.

$$PSV = MSV \times F \qquad 425\text{-}5$$

$$PSV = PST \times VSR \qquad 425\text{-}6$$

Where:

PSV = minimum sampling time, hours

MSV = minimum sample volume, dscm

F = safety factor for detection ($F \geq 1$)

PST = planned sampling time, hours

VSR = volumetric sampling rate, dscm/hour

Typically, when the value of F is one or greater, it is safe to assume that Cr6 will be detected at or above the source target concentration (STC). Greater values of F provide greater assurance. Typically, when the value of F is less than one, it is unsafe to assume that Cr6 will be detected at the source target concentration (STC).

3.5.5 Planned Sampling Time (PST)

The planned sampling time (PST) is calculated using Equation 425-7.

$$PST = MST \times F \qquad 425\text{-}7$$

Where:

PST = planned sampling time, hours

MST = minimum sampling time, hours

F = safety factor for detection ($F \geq 1$)

3.5.6 Pre-Test Calculation of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the reporting limit for emissions of Cr6 from the source. Notice that the SRL is higher than the STC if F is less than one in which case it is unsafe to assume that Cr6 will be detected at the STC.

Equation 425-4 shall be used to calculate the SRL.

$$SRL = \frac{RL}{PSV} \qquad 425\text{-}8$$

Where:

SRL = source concentration reporting limit, ng/dscm

RL = analytical mass reporting limit, ng

PSV = planned sampling volume, dscm

4 BIASES AND INTERFERENCES

4.1 Sample Instability

Chromium is subject to changes in valence state during the time between sampling and recovery. Take all reasonable precautions, some of which are required in various sections of this method, to minimize all influences which may change the valence states of chromium in each sample. Factors which influence such changes are hold time, pH, and other chemical species.

Recovery of trains shall take place within 24 hours of sampling. Storage between recovery and analysis shall be at or below 4C and shall be limited to two weeks.

4.2 Cr6 IC-C Interferences

A high ionic concentration in the sample may overload the chromatographic column, altering the retention time and/or the shape of the chromate peak. Anionic species such as molybdate or vanadate which will react with the 1,5 diphenylcarbazide post-column reagent to form a colored product absorbing at 520-540 nm may obscure or interfere with the quantitation of the chromate peak by coeluting with or overlapping with it, if the concentration of the interfering compounds is sufficiently high. Some known interferences are:

4.2.1 Molybdenum

Molybdenum as a solution of molybdic acid ($H_2MoO_4 \cdot H_2O$) in water produced a peak which eluted at 3.55 minutes when Cr6 was eluting at 4.25 minutes. The Mo^{6+} peak was resolved from a peak representing 50 ng Cr6/mL up to a concentration of approximately 500 µg Mo^{6+}/mL.

4.2.2 Vanadium

Vanadium as a solution of ammonium vanadate (NH_4VO_3) in water produced a broad peak at 2.80 minutes when Cr6 was eluting at 4.25 minutes. This peak was resolved from a peak representing 50 ng Cr6/mL up to a concentration of approximately 10 µg V^{5+}/mL.

4.3 Cr6 M-C Interferences

Molybdenum, mercury and vanadium react with diphenylcarbazide to form a color; however, approximately 20 mg of these elements can be present in a sample without creating a problem. Iron produces a yellow color, but this effect is not measured photometrically at 540 nm.

4.4 Cr GF-AA Interferences

The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters shall be optimized to minimize these effects. If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube shall be cleaned by operating the furnace at higher atomization temperatures.

Nitrogen shall not be used as the purge gas because of a possible CN band interference.

Low concentrations of calcium may cause interferences; at concentrations above 200 mg/L calcium's effect is constant. Calcium nitrate is therefore added to ensure a known constant effect. This step may be omitted if the sample is known to be free of calcium or no analytical interferences are expected.

5 SENSITIVITY

The test method sensitivity is dependent on the parameters chosen during the required pre-test protocol in the **?**PRE-TEST PROTOCOL" section. In general, the higher the planned sampling volume, the better (lower) the test method sensitivity.

5.1 Cr6 IC-C Sensitivity

Based on the procedures given in the "Pre-Test Protocol," an LOD as low as 0.5 ng/mL has been observed; this is not a default value as achievement of such low levels depends upon the skill of the analytical team.

5.2 Cr6 M-C Sensitivity

Based on the procedures given in the "Pre-Test Protocol," an LOD as low as 4.0 ng/mL has been observed; this is not a default value as achievement of such low levels depends upon the skill of the analytical team.

5.3 Cr GF-AA Sensitivity

EPA Method 306, Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations, reports a value of 1.0 ng/mL, based on method 7191 of SW-846. For some sample matrices, the Cr GF-AA sensitivity can be lower than the Cr6 IC-C sensitivity.

6 RANGE

6.1 Cr6 IC-C Range

Using sample loops of 10 uL to 250 uL, the linear range of this procedure without dilution or concentration of the sample is approximately 0.5 ng Cr6/mL to 40 µg Cr6/mL.

6.2 Cr6 M-C Range

A straight line response curve was obtained in the range 0.5 µg Cr6 /50 mL to 3.0 µg Cr6 /50 mL (10 to 60 ng/mL). The range can be expanded to 0.5 to 50 µg/mL, provided that the residuals are less than 10%. For a minimum analytical accuracy of 100 $\pm$ 10 percent, the lower limit of the range is 2 µg/100mL. The upper limit can be extended by appropriate dilution or by using a smaller cell path length after recalibration for the smaller cell.

6.3 Cr GF-AA Range

EPA Method 306, Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations, reports an optimum range of 5 to 100 ng/mL, based on method 7191 of SW-846. For some sample matrices, the Cr GF-AA range can be broader than the Cr6 IC-C range.

7 EQUIPMENT

All surfaces which may come in contact with sample shall be glass, quartz, Teflon, or other similarly non-metallic (stainless steel may be a source of chromium contamination) inert material.

Although Teflon is not the required material of construction for sampling train components, it can be used to reduce problems with equipment contamination and cleaning.

Any other sampling apparatus which, after review by the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

7.1 Sampling Equipment

Except where otherwise noted in this method, same as CARB Method 5, Section 2.1. Exceptions include a glass nozzle, a glass lined stainless steel probe, 0.1 N NaOH in the first two impingers, a Teflon-coated glass fiber filter, and a silica gel moisture trap after the filter. As shown in Figure 1, sample flow shall be through the probe first, then the impingers, and then the filter.

7.2 Recovery Equipment

Except where otherwise noted in this method, same as CARB Method 5, Section 2.2.

7.3 Analytical Equipment

7.3.1 Cr6 IC-C Analytical Equipment

The following system has been found suitable for hexavalent chromium analysis as described in this procedure. Specifications, analytical ranges, and detection limits were determined using this system. An equivalent system may be used so long as it is demonstrated to be capable of separating and detecting hexavalent chromium, and the sensitivity and precision of the system is determined to be adequate.

7.3.1.1 DIONEX Ion Chromatography System 4000i (or equivalent), including:

Gradient Pump Module

Advanced Chromatography Module

Variable Wavelength Detection Module

Automated Sampler

Eluant Degas Module

Advanced Computer Interface

IBM-AT Compatible Computer, running the DIONEX Autoion 450 (or equivalent) Data System Chromatography Software

Chromatographic Columns
Organic compound guard column: DIONEX MPIC-NG1 (or equivalent) neutral guard column.

Anion guard column (can also used as a preconcentrater column): DIONEX HPIC-AG7 (or equivalent) high-capacity anion guard column.

Separator column: DIONEX HPIC-AS7 or equivalent high-capacity anion separator column.

7.3.1.2 Post-Column Reagent System, including:

Pressurized reagent reservoir.

120 cm Packed Bed Reaction Coil.

7.3.2 Cr6 M-C Analytical Equipment

7.3.2.1 100 mL beakers

7.3.2.2 Filtration Apparatus

Vacuum unit constructed of glass, to accommodate sintered glass funnels. Medium porosity filter paper is optional. Wherever filtering is specified, centrifuging may also be performed at the analyst's option.

7.3.2.3 Volumetric Flasks

100-mL and other appropriate volumes.

7.3.2.4 Hot Plate

7.3.2.5 Pipettes

Assorted sizes, as needed.

7.3.2.6 Spectrophotometer

To measure absorbance at 540nm.

7.3.3 Cr GF-AA Analytical Equipment

7.3.3.1 Philips Beakers

Borosilicate, 125mL, with digestion covers.

7.3.3.2 Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp.

7.3.3.3 Graphite Furnace

Any graphite furnace device with the appropriate temperature and timing controls.

7.3.3.4 Strip Chart Recorder

A recorder is recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

8 PREPARATION OF EQUIPMENT

The following sections specify a recommended cleaning procedure for sampling equipment and extremely stringent cleaning performance criteria. An alternative cleaning procedure is allowed providing that experimental documentation is provided which demonstrates that the alternative cleaning procedure has been established and is at least as effective at achieving the cleaning performance criteria as the recommended procedure.

The chosen cleaning procedure shall be applied to all equipment surfaces (not only the probe surfaces) which can come in contact with the sample.

8.1 Recommended Cleaning Procedure

All surfaces which can come in contact with sample shall be glass, Teflon, or other similarly non-metallic (even stainless steel may be a source of chromium contamination) inert material and shall be prewashed with detergents, soaked in 1:1 HNO_3 for several hours, rinsed with Type II water, and finally rinsed with 0.1 N NaOH batch solution. For awkward objects, such as long glass probes, soaking may be replaced by careful wiping.

Probes are generally the most difficult sampling apparatus to clean. Therefore, before use in sampling, to ensure that sampling equipment is clean and free of chromium contamination, apparatus which may come in contact with sample shall be cleaned and a sample of the final rinse for each probe shall be analyzed for Cr (total chromium). If Cr is detected in the final rinse, each probe shall be re-cleaned until a sample of the final rinse contains no detectable Cr. "Cr GF-AA ANALYTICAL PROCEDURES" shall be followed for this contamination check.

8.2 Alternative Cleaning Procedure

If the specified glass probes are in short supply, the recommended cleaning procedure could double the number of days necessary to complete a series of tests.
Time can be saved by using the following options:

8.2.1 Development, Testing, and Documentation

An alternative cleaning procedure may be used if it is developed, tested, and documented as achieving the objective of no detectable chromium in the last probe cleaning rinse. Testing and documentation shall include: a pre-test visit to the intended site, collection of samples from an intended test point with the highest expected concentration of chromium, trials of other cleaning procedures, and documentation of those alternative cleaning procedures which pass the contamination check of the "Recommended Cleaning Procedure".

8.2.2 Advanced Preparation

The best protection against lost time is to procure enough pre-cleaned equipment before a field trip so that no equipment needs to be re-cleaned and re-used during field sampling. Procure extra pre-cleaned equipment to allow for breakage, etc.

9 REAGENTS

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

9.1 Sampling Reagents

9.1.1 Method 5 Reagents

Except where otherwise noted in this method, same as CARB Method 5, Section 3.1, except Teflon-coated glass fiber filters are used, and 0.1 N NaOH is used in the first two impingers.

9.1.2 Batch of 0.1N NaOH Solution, Analytical Reagent Grade

The most important purpose of this solution is to maintain hexavalent chromium in a high pH solution so that it is not reduced to trivalent chromium. In particular, liquid samples must be taken and transported at a pH of 8.0 or higher.

Any other solution which can meet this and the other performance specifications of this method is also acceptable.

See "PREPARATION OF REAGENTS."

9.2 Recovery Reagents

Except where otherwise noted in this method, same as CARB Method 5, Section 3.2.

9.3 Cr6 IC-C Analytical Reagents

Unless otherwise indicated, all chemicals shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. All reagents shall be analyzed before testing is begun using the IC-C system to be employed in the analysis of the samples, and the Cr6 concentration shall be less than the detection limit.

9.3.1 Batch of 0.1N NaOH Solution

See "PREPARATION OF REAGENTS."

9.3.2 Water

All water used in this procedure shall, at minimum, conform to the specifications of American Society for Testing and Materials (ASTM) Type II reagent water as specified in ASTM Test Procedure D 1193. Use of ASTM Type I reagent water shall be an acceptable alternative.

9.3.3 Eluent

Dissolve 33 g of ammonium sulfate in water in a 1 L Class A volumetric flask. Add 6.5 mL of 29% ammonium hydroxide and make to volume. The concentration of the prepared eluent is 250 mM $(NH_4)_2SO_4$ and 100 mM NH_4OH.

9.3.4 Post-Column Reagent

Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 mL of glass distilled HPLC grade methanol. Add to approximately 500 mL of degassed or nitrogen purged or helium purged water containing 28 mL of 96-98% sulfuric acid, and make to 1 L with degassed or nitrogen purged or helium purged water. High purity sulfuric acid such as EM Science Suprapur grade or JT Baker Ultrex grade is recommended. The stability of the post-column reagent is enhanced by preparing it in a nitrogen atmosphere, pressurizing the reagent reservoir with nitrogen, and shielding it from light.

9.3.5 Cr6 Stock Solution

Prepare a standard solution containing 1000 µg Cr6 /mL as a solution of potassium dichromate in water. Use analytical reagent grade $K_2Cr_2O_7$ which has been dried at 105^o C for at least one hour. Dissolve 2.8289 g of the dried $K_2Cr_2O_7$ in water in a class A volumetric flask and make to volume with water. Alternatively, obtain a chromate standard solution in water prepared specifically for use in ion chromatography.

Storage shall be at or below 4^{o}C and shall be limited to four weeks.

9.3.6 Regenerant Solution for the DIONEX MPIC-NG1 Guard Column (or equivalent)

In this application, the DIONEX MPIC-NG1 guard column (or equivalent) is used to trap organic compounds which could adversely affect the anion chromatographic columns. The trapped organic compounds shall be flushed from the column periodically using a 70-90% solution of acetonitrile or methanol in water.

9.4 Cr6 M-C Analytical Reagents

9.4.1 Batch of 0.1N NaOH Solution

See "PREPARATION OF REAGENTS."

9.4.2 Type II Water

Type II water is deionized and distilled, meeting American Society for Testing and Materials (ASTM) specification for type reagent - ASTM Test Method D 1193-77. The water shall be monitored for impurities.

9.4.3 Potassium Dichromate Stock Solution

Dissolve 2.829 g of analytical reagent grade potassium dichromate ($K_2Cr_2O_7$) in water, and dilute to 1 liter (1 mL = 1000 µg Cr6).

9.4.4 Potassium Dichromate Standard Solution

Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 100 µg Cr6 with water.

9.4.5 Sulfuric Acid, 6N, Analytical Reagent Grade

Dilute 166 mL sulfuric acid to 1000 mL in water.

9.4.6 Diphenylcarbazide Solution, Analytical Reagent Grade

Dissolve 0.5 g of 1,5-diphenylcarbazide in 100 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

9.4.7 0.1% Potassium Permanganate Solution

Analytical Reagent Grade

9.4.8 0.01% Potassium Permanganate Solution

Analytical Reagent Grade

9.5 Cr GF-AA Analytical Reagents

9.5.1 Batch of 0.1N NaOH Solution

See "PREPARATION OF REAGENTS."

9.5.2 ASTM Type II Water (ASTM D1193)

9.5.3 Concentrated Nitric Acid

Reagent preparation shall use Ultrex (or equivalent) grade HNO_3.

Glassware cleaning shall use ACS reagent grade HNO_3.

9.5.4 Hydrogen Peroxide (30%) (Optional), Analytical Reagent

9.5.5 Matrix Modifier

Follow manufacturer's recommendations, when interferences are suspected.

9.5.6 Total Chromium Standard Stock Solution (1000 mg/L)

Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, Fisher Scientific, etc.) and verify by comparison with a second standard, or dissolve 2.829 g of Potassium Dichromate ($K_2Cr_20_7$, analytical reagent grade) in Type II water and dilute to 1 liter in a volumetric flask.

9.5.7 Total Chromium Working Standards

All total chromium preparations injected for analysis shall be prepared to contain 1.0% (v/v) $HN0_3$. The zero standard shall be 1.0 % (v/v) HNO_3.

10 PREPARATION OF REAGENTS

10.1 Preparation of Reagents for Sampling

10.1.1 Batch of 0.1N NaOH Solution, Analytical Reagent Grade

The same batch of 0.1N NaOH solution shall be used for impinger sampling, sample recovery, preparation, extraction, and analysis.

This is necessary to avoid the use of different 0.1N NaOH solutions with different levels of contamination, especially of Cr6, but also of analytical interferents.

Therefore, sampling and analytical personnel shall coordinate their plans so that all steps in sampling and analysis use the same batch of solution which will be prepared fresh for each source test. Typically, dissolve 4.0 g NaOH in water in a 1 liter volumetric flask and dilute to the mark. Repeat, as necessary, so that a single batch of sufficient volume is prepared to serve all of the needs of sampling and analysis. Store the solution in a tightly capped polyethylene bottle.

The most important purpose of this solution is to maintain hexavalent chromium in a high pH solution so that it is not reduced to trivalent chromium. In particular, liquid samples must be taken and transported at a pH of 8.0 or higher.

Any other solution which can meet this and the other performance specifications of this method is also acceptable.

10.1.2 Removal of Reducing Agents in the Reagents

The 0.1 N NaOH extraction solution and the 6N sulfuric acid solution may contain small amounts of reducing agents that can react with the hexavalent chromium. Potassium permanganate ($KMnO_4$) is added to these reagents in order to neutralize these reducing agents.

Determine the amount of $KMnO_4$ needed as follows:

Pipette 3 mL of the extraction solution into cuvettes A and B. Use cuvette A as a sample cell and cuvette B as a reference cell. Zero the instrument at 528 nm with both cuvettes. Wait 10 minutes. Add an adequate amount (uL) of 0.01% potassium permanganate solution to cuvette A so that after 10 minutes a slight change in absorbance is observed. This step may have to be repeated a number of times in order to determine the required amount of potassium permangante.

From the change in absorbance, calculate the amount of potassium permanganate per unit volume needed to neutralize the reducing agents found in the reagents.

Determine the amount of higher concentration 0.1% potassium permanganate solution needed to treat the volume of reagent. Pipette this amount of 0.1% $KMnO_4$ into the reagents.

Repeat this procedure with the 6N sulfuric acid solution.

10.2 Preparation of Reagents for Recovery

The same batch of 0.1N NaOH solution shall be used for impinger sampling, sample recovery, preparation, extraction, and analysis.

10.3 Preparation of Reagents for Analysis

The same batch of 0.1N NaOH solution shall be used for impinger sampling, sample recovery, preparation, extraction, and analysis.

11 CALIBRATION PROCEDURE

11.1 Sampling Calibration Procedure

Perform all of the calibrations described in CARB Method 5, Section 5, with any modifications appropriate for this method.

11.2 Recovery Calibration Procedure

Follow the appropriate analytical calibration procedure.

11.3 Cr6 IC-C Analytical Calibration Procedure

Inject a series of Cr6 calibration standards which brackets the sample concentrations. Also, use a zero standard. Typically, 4 to 6 calibration standards will be sufficient to establish the calibration curve. The recommended procedure is to inject one series of calibration standards before the samples, to establish that the system is working properly and has reached equilibrium so that a linear response is attained. A second set of calibration standards is injected at the end of the analytical run to confirm constancy of response throughout the run. If the peak areas or peak heights of the two sets of calibration standards differs by more than 5% the run shall usually be repeated. If any drift in response which may have occurred is within acceptable limits, use the concentration and response values of the two sets of calibration standards to establish a calibration curve which is used to

quantitate the Cr6 concentration in the samples.

Inject a check standard prior to the tenth run of the instrument since its last calibration run.

11.4 Cr6 M-C Analytical Calibration Procedure

(1) Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials shall be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer shall read correctly within $\pm$5 nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 540 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

(2) Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 530 and 550 nm using a 50 µg Cr6 standard solution in the sample cell and a reagent blank solution in the reference cell. If a peak does not occur, the spectrophotometer is malfunctioning and shall be repaired. When a peak is obtained within the 530 to 550 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the reagent blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum differences in absorbance between the standard and the reagent blank occurs.

(3) Either (1) run a series of 4 to 6 chromium calibration standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) if matrix effects require the method of standard additions (see 17.2.1), plot added concentration versus absorbance.

(4) Freshly make up each standard for Cr6 in a separate 50 mL volumetric flask starting with 35 mL of the same batch of NaOH solution reserved for its sample set. Then add an appropriate amount of Cr6 to each calibration standard, starting with none for the zero standard. Then add 6N sulfuric acid and diphenylcarbazide solution in the same manner as in sample preparation.

(5) Inject a check standard prior to the tenth run of the instrument since its last calibration run.

11.5 Cr GF-AA Analytical Calibration Procedure

(1) Calibration standards for total chromium shall start with 1% v/v HNO_3 with no chromium for the reagent blank with appropriate increases in total chromium concentration in the other calibration standards. The calibration standards shall be prepared following the steps outlined for sample preparation in the analytical procedures.

(2) Check standards shall be prepared in the same manner as calibration standards. Check standards shall be prepared separately and independently from the calibration standards and shall serve to protect against errors in the preparation of the calibration standards.

(3) Either (1) run a series of chromium standards and reagent blanks and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) if matrix effects require the method of standard additions (see 17.2.1), plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

(4) Re-run the lowest calibration standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or a significant change in the signal for the standards indicates that the tube shall be replaced.

(5) Duplicates, spiked samples, and check standards shall be routinely analyzed. This requirement is further specified in the quality assurance/quality control procedures.

(6) Calculate Cr concentrations (1) from a calibration curve, or (2) by the method of standard additions, or (3) directly from the instrument's concentration readout. All dilution or concentration factors shall be taken into account.

(7) Calibration curves shall be composed of a minimum of a reagent blank and three total chromium standards. A calibration curve shall be made for every batch of samples, unless check standards remain within 10% of the last calibration curve.

(8) Dilute samples with reagent blank solution if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

12 SAMPLING PROCEDURE

At all times during sampling and transport of samples, the pH of the impinger solutions shall be maintained above a pH of 8.0 as determined by the use of a clean rod and color indicating paper for pH.

12.1 Method 5 Sampling Procedure and Exceptions

Except where otherwise indicated in this method, all samples are collected from the source by use of CARB Method 5. Exceptions include a glass nozzle, a glass lined stainless steel probe, 0.1 N NaOH in the first two impingers, and a Teflon-coated glass fiber filter. As shown in Figure 1, sample flow shall be through the probe first, then the impingers, and then the filter.

12.2 Sampling Runs

The performance of this test method shall include three or more sampling runs.

The performance criteria documented in the pre-test protocol shall be used by the test crew to maximize, in the test crew’s judgement, the degree to which each sampling run occurs during an interval or intervals of time during which the source facility operations are representative of the conditions intended by the pre-test protocol.
A narrative field log shall be kept by the sampling crew to document observations which subsequently can be used by others to evaluate the degree to which the source facility operations are representative of the conditions intended by the pre-test protocol.

12.3 Field Blank Run

The performance of this test method shall include one or more field blank runs. Every step of the test method shall be followed for each field blank run with the exception that sample gas shall not be withdrawn from the source facility by the field blank train.

13 RECOVERY PROCEDURE

At all times during sampling and transport of samples, the pH of the probe rinse and impinger solutions shall be maintained above a pH of 8.0 as determined by the use of a clean rod and color indicating paper for pH.

13.1 Silica Gel Recovery

For stack gas moisture determination, weigh the spent silica gel or silica gel plus impinger to the nearest 0.5 g using a balance. This step may be conducted in the field.

13.2 Probe Recovery

Rinse the probe with at least 100 mL of 0.1 N NaOH ; measure and record the probe rinse volume and store the probe rinse in Container 1. Transport the probe rinse to a clean room or to a site with laboratory conditions. Split the probe rinse into two approximately equal volumes; measure and record the volume of each split. Label one split for Cr6 analysis and label the other split for total Cr analysis.

13.3 Impinger and Filter Recovery

This method does not require impinger rinses.

The sampling and analytical personnel shall discuss the expected sample concentrations and the analytical limits of detection for hexavalent and total chromium. The impinger catch and filter shall be handled one of two ways depending on these expectations as directed below in the "Higher Concentrations" and "Lower Concentrations" sections below.

13.3.1 Higher Concentrations

If it is not considered important to minimize the dilution of any sample component, then the contents of both impingers (~200 mL total) shall be combined and stored in container 2. (Measure the volume.) As soon as possible, the filter is transported in a filter container to a site with laboratory conditions where it shall be extracted in all of the impinger solution from Container 2. The extraction shall include shaking for a minimum of 30 minutes. The alkaline impinger medium will retard reduction of hexavalent chromium.
Split the extract solution with half saved for hexavalent chromium analysis and half saved for total chromium analysis. Each sample split is ~100 mL. (Measure the volumes.)

13.3.2 Lower Concentrations

If it is considered important to minimize the dilution of any sample component, then the

contents of each impinger (~100 mL each) may be stored in Containers 2 and 3. (Measure the volumes.) The filter shall be extracted in only one of the impinger contents, whichever is suspected to have the higher concentration. The extraction shall include shaking for a minimum of 30 minutes. The contents of the first impinger are stored in Container 2 and those of the second impinger in Container 3. Whichever impinger contents are not used for extraction shall be handled as a third sample recovery requiring separate analyses.

Split the extract solution with half saved for hexavalent chromium analysis and half saved for total chromium analysis. Each sample split is ~50 mL. (Measure the volumes.)

14 Cr6 IC-C ANALYTICAL PROCEDURES

The ion chromatograph shall be set up and operated according to the instructions of the manufacturer of the instrument. A generalized diagram of the system configuration is shown in Figure 1.

14.1 IC-C Preparation

If any of the samples are suspected to contain particulate material, they shall be filtered through a 0.45 µm or smaller pore size membrane filter prior to analysis.

14.2 IC-C Analysis

14.2.1 Eluent Flow Rate

Adjust the eluent flow rate to 1.5 mL/minute.

14.2.2 Post Column Reagent Flow Rate

Adjust the post column colorimetric reagent flow rate to 0.5 mL/minute. The flow rate from the outlet line of the detector with the post column reagent delivery system on shall be confirmed to be 2.0 mL/minute.

14.3 IC-C Detection

Absorbance of the colored product formed by the reaction of the 1,5 diphenylcarbazide colorimetric reagent with Cr6 has been shown to be maximized at 540 nm for the system described and with the reagents used. The optimum wavelength for detection of the colored Cr6 derivative may vary depending on the source and batch of reagents used, and may be determined experimentally for each system by running a series of Cr6 standards at a range of wavelengths of detection. Alternatively, or in addition, the peak of the absorption band of the colored product can be determined by preparing a Cr6 standard in eluent, adding 1 part of the colorimetric reagent to 3 parts of the Cr6 spiked eluent, and recording a plot of the absorption band using a scanning spectrophotometer. The absorption band of the colored product is relatively broad, and for most applications an adequate response can be attained at wavelengths of 530-540 nm without the necessity of determining the exact wavelength of maximum absorbance.

15 Cr6 M-C ANALYTICAL PROCEDURES

15.1 M-C Preparation

15.1.1 Cr6 Reagent Blank Preparation

For each preparation, transfer 35 mL of solution to a 100 mL beaker, adjust the pH to 1.0 $\pm$ 0.2 with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide solution, dilute to volume with water in a 50 mL volumetric flask, and let color develop for 10 minutes.

15.1.2 Hexavalent Chromium Sample Preparation

For each preparation, transfer 35 mL of solution to a 100 mL beaker, adjust the pH to 1.0 $\pm$ 0.2 with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide solution, dilute to volume with water in a 50 mL volumetric flask, and let color develop for 10 minutes. (This leaves at least 15 mL of sample split for further analyses. The total volume of sample split shall be known at this point.)

15.2 M-C Analysis

(1) Filtration shall be an option for the analyst at this point, depending on the turbidity of the prepared sample. Medium retention filter paper shall be used. The filter paper shall be pre-wetted with a few mL of reagent blank and sample preparation. This will prime the filter so that it won't absorb color complex.

(2) Transfer a portion of the filtered preparation into a 5 cm absorption cell.

(3) Measure the absorbance at the optimum wavelength of 540 nm.

(4) Subtract the sample blank absorbance reading to obtain a net reading.

(5) If the absorbance reading of a sample preparation exceeds the calibration range, dilute with reagent blank or re-measure using less of the sample preparation. (There shall be about 15 mL remaining at this point.)

16 Cr GF-AA ANALYTICAL PROCEDURES

16.1 Cr GF-AA Preparation

16.1.1 Cr Reagent Blank Preparation

For total chromium, the reagent blank is an aliquot of 1% HNO_3.

16.1.2 Cr Sample Preparation

In a beaker, add 10 ml of concentrated nitric acid to the sample aliquot taken for analysis. Cover the beaker with a digestion coverglass . Place the beaker on a hot plate and reflux the sample down to near dryness. Add another 5 mL nitric acid to complete digestion. Reflux the sample volume down to near dryness.

Wash down the beaker walls and digestion cover with distilled water and filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration shall be done only if there is concern that insoluble materials may clog the nebulizer. Adjust the volume to 50 mL or a predetermined value based on the expected Cr concentrations. The final concentration of HNO_3 in the solution shall be 1 % (v/v). The sample is now ready for analysis. The applicability of a sample preparation technique shall be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

16.2 Cr GF-AA Analysis

16.2.1 Total Chromium Analysis

(1) The 357.9-nm wavelength line shall be used.

(2) Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

(3) Furnace parameters suggested by the manufacturer shall be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters shall be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

(4) Inject a measured uL aliquot of preparation into the furnace and atomize. If the concentration found exceeds the calibration range, the sample shall be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

(5) Subtract a reagent blank reading from a sample reading to obtain a net reading.

17 QUALITY ASSURANCE / QUALITY CONTROL (QA/QC)

17.1 Sampling QA/QC

17.1.1 Pre-Test Protocol

At a minimum, the QA/QC of the pre-test protocol shall include:

(1) target concentration (TC) chosen by consent of interested parties

(2) limit of detection (LOD) based on four or more lab blanks

(3) planned sampling flow rate

(4) planned sampling time

17.1.2 Test Protocol

At a minimum, the QA/QC of the test protocol shall include:

(1) three or more sampling runs

(2) one or more field blanks

17.2 Cr6 IC-C Analytical QA/QC

17.2.1 Check for Matrix Effects on the Cr6 Results

As the analysis for Cr6 by colorimetry is sensitive to the chemical composition of the sample (matrix effects), the analyst shall check at least one sample from each source using the following method: Obtain two equal volume aliquots of the same sample solution. The aliquots shall each contain between 6 and 10 µg of Cr6 (less if not possible). Spike one of the aliquots with an aliquot of standard solution that contains between 6 and 10 µg of Cr6. Now analyze both the spiked and unspiked sample aliquots as described in "Cr6 IC-C ANALYTICAL PROCEDURES" above. Next, calculate the Cr6 mass, in µg, in the aliquot of the unspiked sample solution, Cs, by using Equation 425-9:

$$Cs = Ca \times \left(\frac{As}{At - As} \right) \qquad 425\text{-}9$$

Where:

Cs = Cr6 in the unspiked sample solution, µg.

Ca = Cr6 in the standard solution, µg.

As = absorbance of the unspiked sample solution.

At = Absorbance of the spiked sample solution.

Volume corrections will not be required since the solutions as analyzed have been made to the same final volume. If the results of this method used on the single source sample do not agree to within 10 percent of the value obtained by the routine spectrophotometric analysis, then reanalyze all samples from the source using the method of standard additions procedure.

17.2.2 Blanks

Four or more lab blanks shall be analyzed before any performance of this test procedure.

For each set of three field sampling runs, one or more associated field blank runs shall be analyzed.

17.2.3 Duplicates

For each set of three field sampling runs, one or more samples shall be injected in duplicate.

If the difference between the determined Cr6 concentrations of the sample duplicates exceeds 5% of their mean value, the results for the associated sampling runs shall be considered invalid.

17.3 Cr6 M-C Analytical QA/QC

17.3.1 Check for Matrix Effects on the Cr6 Results

As the analysis for Cr6 by colorimetry is sensitive to the chemical composition of the sample (matrix effects), the analyst shall check at least one sample from each source using the following method: Obtain two equal volume aliquots of the same sample solution. The aliquots shall each contain between 6 and 10 µg of Cr6 (less if not possible). Spike one of the aliquots with an aliquot of standard solution that contains between 6 and 10 µg of Cr6. Now treat both the spiked and unspiked sample aliquots as described in Section 15.1.2 above. Next, calculate the Cr6 mass, in µg, in the aliquot of the unspiked sample solution, Cs, by using Equation 425-10:

$$Cs = Ca \times \left(\frac{As}{At - As} \right) \qquad 425\text{-}10$$

Where:

Cs = Cr6 in the unspiked sample solution, µg.

Ca = Cr6 in the standard solution, µg.

As = absorbance of the unspiked sample solution.

At = Absorbance of the spiked sample solution.

Volume corrections will not be required since the solutions as analyzed have been made to the same final volume. If the results of this method used on the single source sample do not agree to within 10 percent of the value obtained by the routine spectrophotometric analysis, then reanalyze all samples from the source using the method of standard additions procedure.

17.4 Cr GF-AA Analytical QA/QC

(1) Employ a minimum of one matrix-matched sample blank per sample batch to determine if contamination or memory effects are occurring.

(2) Test the system with check standards after approximately every 15 samples.

(3) Run one duplicate sample for every 10 samples, providing there is enough sample for duplicate analysis. A duplicate sample is a sample brought through the whole sample preparation. (See "Cr GF-AA ANALYTICAL PROCEDURES")

(4) Spiked samples or standard reference materials shall be used daily to ensure that correct procedures are being followed and that all equipment is operating properly. This will serve as a check on calibration standards, too.

(5) Whenever sample matrix problems are suspected, the method of standard additions shall be used for the analysis of all extracts, or whenever a new sample matrix is being analyzed.

(6) All quality control data shall be maintained for easy reference or inspection.

18 RECORDING DATA

18.1 Data Records

At a minimum, the tester shall maintain records of field, laboratory, and office data sufficient to support recalculation of reported results by an auditor.

18.2 Narrative Account

At a minimum, the tester shall maintain a narrative account characterizing source and testing operations during the source testing and analysis. In the narrative, include the means by which the values of the source and testing parameters, chosen for the pre-test protocol, were maintained; also include a narrative of unplanned or unexpected events which caused a departure from the chosen values.

19 CALCULATING RESULTS

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

19.1 Total Cr6 in the Sample Train (mCr6)

Calculate and report mCr6, the total µg Cr(VI) in the sample train. This can be obtained from the calibration curve or from the method of standard additions. Note that mCr6 is the sum of the masses of hexavalent chromium analyses performed on all sample portions. Also take into account any dilutions when calculating mCr6.

Calculations shall include only sample portions which have values above the LOD.

Do not subtract the LOD from the sample train values.

19.1.1 Cr6 IC-C Analytical Calculations

Report these calculations based on net values, as determined by the instrument.

If instrument blank values are not automatically taken and subtracted by the instrument, report these calculations based on net values, and report all instrument blank values, too.

These are zero standards.

See below for determination of net values.

19.1.2 Cr6 M-C Analytical Calculations

Report these calculations based on net values using Equation 425-11. Report all instrument blank values, too.

Net Value = Sample Train Component Value - Zero Blank Value 425-11

19.2 Total Cr in the Sample Train (mCr)

Calculate and report mCr, the total µg of chromium in the sample train. This can be obtained from the calibration curve or from the method of standard additions. Note that mCr is the sum of the masses of total chromium analyses performed on all sample portions. Also take into account the necessary dilutions when calculating out mCr.

Calculations shall include only sample portions which have values above the LOD.

Do not subtract the LOD from the sample train values.

Report these calculations based on net values, and report all instrument blank values, too.

See above for determination of net values.

19.3 Method 5 Testing Parameters

Except where otherwise noted in this method, follow the procedures of ARB Method 5 to determine:

(1) Standard Volume of Gas Sample ≡ (Vsample)

Typical units for Vsample are dry standard cubic meters, dscm.

(2) Isokinetic Variation

(3) Standard Volumetric Flow Rate of Stack Gas ≡ (Qstack)

Typical units for Qstack are dry standard cubic meters per hour, dscm/hour.

19.4 Cr6 Mass Emission Concentration ≡ Cr6 MEC

Calculate and report the Cr6 mass emission concentration in the stack gas, dry basis, corrected to standard conditions, using Equation 425-12:

$$\text{Cr6 MEC} = \text{mCr6} \div \text{Vsample} \qquad \text{425-11}$$

Where:

Cr6 MEC = Cr6 concentration in the stack gas, ng/dscm

mCr6 = Cr6 mass in the sampling train, ng

Vsample = stack gas volume sampled, dscm

19.5 Cr6 Mass Emission Rate ≡ Cr6 MER

Calculate and report the Cr6 mass emission rate in the stack gas, dry basis, corrected to standard conditions, using Equation 425-13:

$$\text{Cr6 MER} = \text{Cr6 MEC} \times \text{Qstack} \qquad \text{425-12}$$

Where:

Cr6 MER = Cr6 concentration in the stack gas, ng/dscm

mCr6 = Cr6 mass in the sampling train, ng

Vsample = stack gas volume sampled, dscm

19.6 Cr Mass Emission Concentration ≡ Cr MEC

Calculate and report the Cr mass emission concentration in the stack gas, dry basis, corrected to standard conditions, using Equation 425-14:

$$\text{Cr MEC} = \text{mCr} \div \text{Vsample} \qquad \text{425-13}$$

Where:

Cr MEC = Cr concentration in the stack gas, ng/dscm

mCr = Cr mass in the sampling train, ng

Vsample = stack gas volume sampled, dscm

19.7 Cr Mass Emission Rate = Cr MER

Calculate and report the Cr mass emission rate in the stack gas, dry basis, corrected to standard conditions, using Equation 425-15:

$$\text{Cr MER} = \text{Cr MEC} \times \text{Qstack} \qquad \text{425-14}$$

Where:

Cr MER = Cr concentration in the stack gas, ng/dscm

mCr = Cr mass in the sampling train, ng

Vsample = stack gas volume sampled, dscm

20 REPORTING RESULTS

20.1 Calculated Results

At a minimum, the tester shall report all calculated results required above. Also, as required by the end user of the test results, the tester shall include specified data records, as described above.

Clearly distinguish sample runs for which Cr6 or Cr were DETECTED above the LOD from sample runs for which Cr6 or Cr were NOT DETECTED above the LOD.

20.2 Narrative Account

At a minimum, the tester shall report a narrative account characterizing source and testing operations during the source testing and analysis. In the narrative, include the means by which the values of the source and testing parameters, chosen for the pre-test protocol, were maintained; also include a narrative of unplanned or unexpected events which caused a departure from the chosen values.

20.3 Final Calculation of Source Reporting Limit (SRL)

Equation 425-14 shall be used to calculate the SRL. This equation is adapted from the pre-test protocol; actual values shall be substituted for the pre-test values.

$$SRL = \frac{ARL}{ASV} \qquad 425\text{-}15$$

Where:

SRL = source concentration reporting limit, ng/dscm

ARL = actual reporting limit, ng

ASV = actual sample volume, dscm

21 ALTERNATIVE TEST METHODS

21.1 Direct Measurement of Gas Volumes through Pipes and Small Ducts

Air Resources Board Method 2A may be used, where applicable, as an alternative to pitot tube methods specified in Method 5, as referenced herein.

21.2 Other Impinger Solutions (Instead of NaOH)

0.1 N KOH may be substituted for 0.1 N NaOH in the impinger solution. Other substitutions, e.g. $NaHCO_3$, may be made provided that at all times during sampling and transport of samples, the pH of the impinger solutions shall be maintained above a pH of 8.0 as determined by the use of a clean rod and color indicating paper for pH.

21.3 Total Chromium Determination by Flame Atomic Absorption Spectroscopy

For high total chromium concentrations which are within the detection range of flame atomic absorption spectroscopy, this analytical method may be used instead of the furnace type method specified in these pages. This option applies only to the analysis of total chromium. The remainder of the test method shall be performed as specified.

21.4 Other Methods

Alternative test methods may be used provided that they are equivalent to Method 425 and approved in writing by the Executive Officer of the California Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

22 REFERENCES

(1) EPA Method 5, Determination of Particulate Emissions from Stationary Sources, CFR 40, Part 60, Appendix A.

(2) (Draft) Laboratory and Field Evaluations of Methodology for Determining Hexavalent Chromium Emissions from Stationary Sources; Prepared by: Anna C. Carver, Entropy Environmentalists, Inc., Research Triangle Park, NC 27709; EPA Contract No. 68-02-4550; Prepared for: Dr. Joseph E. Knoll, United States Environmental Protection Agency, Quality Assurance Division, Research Triangle Park, North Carolina 27711, UNDATED.

23 FIGURES

The following figures summarize features of this method:

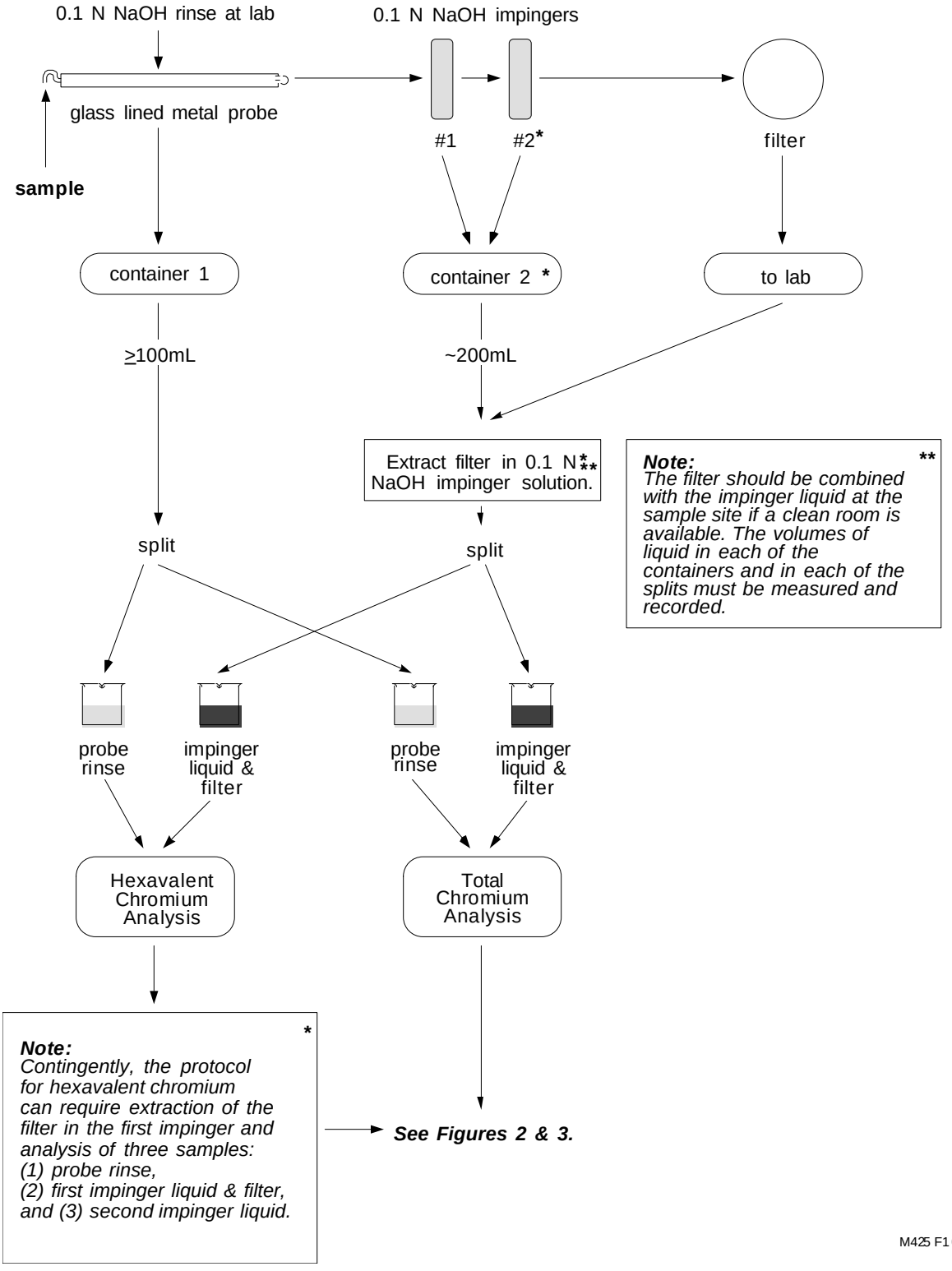
Figure 1.
Sample Collection and Recovery for Hexavalent and Total Chromium

Figure 2.
Hexavalent Chromium Analysis

Figure 3
Total Chromium Analysis

Figure 1

SAMPLE COLLECTION AND RECOVERY FOR HEXAVALENT AND TOTAL CHROMIUM



M425 F1 05/95 Loop

Figure 2

HEXAVALENT CHROMIUM ANALYSIS

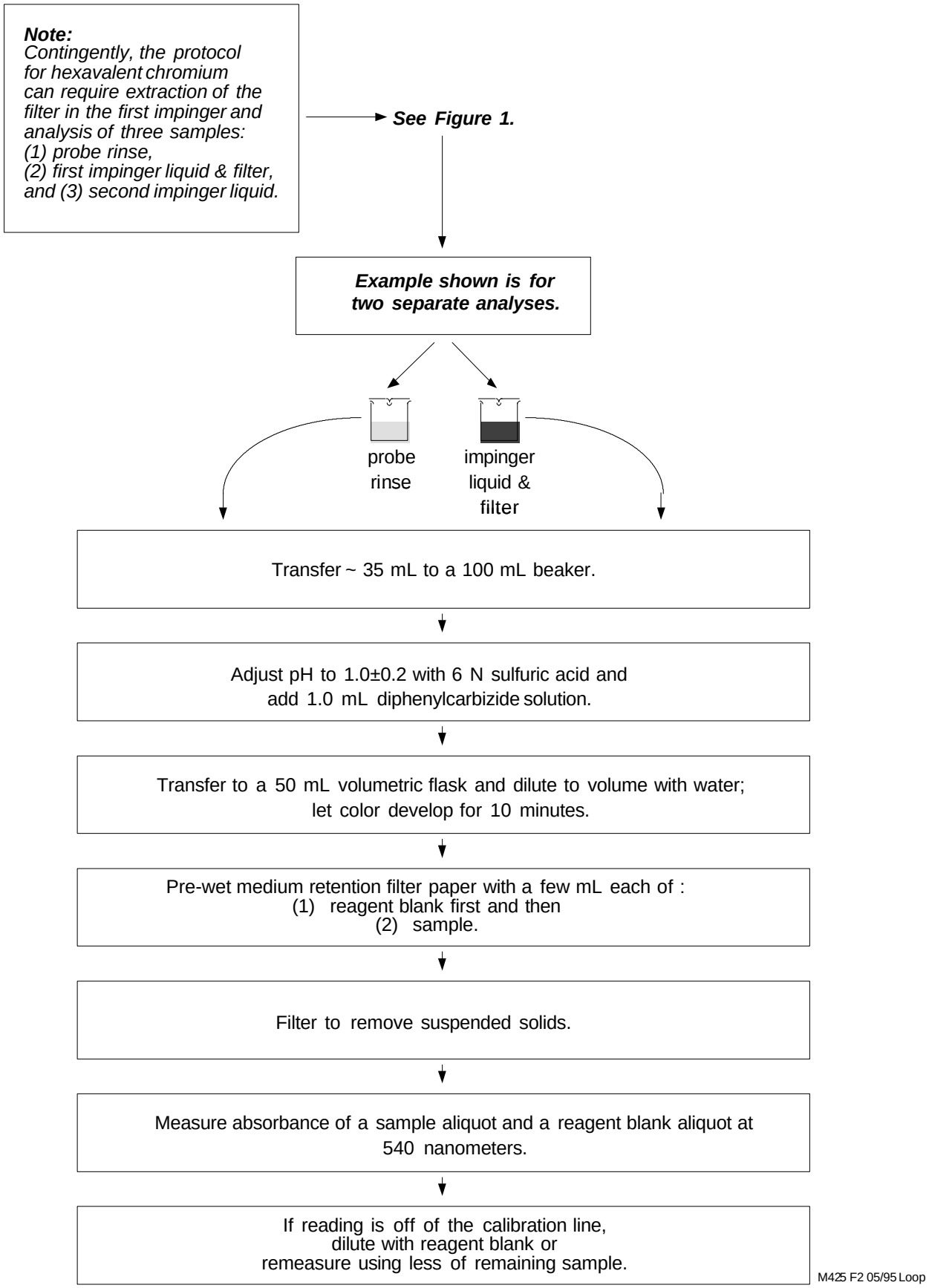


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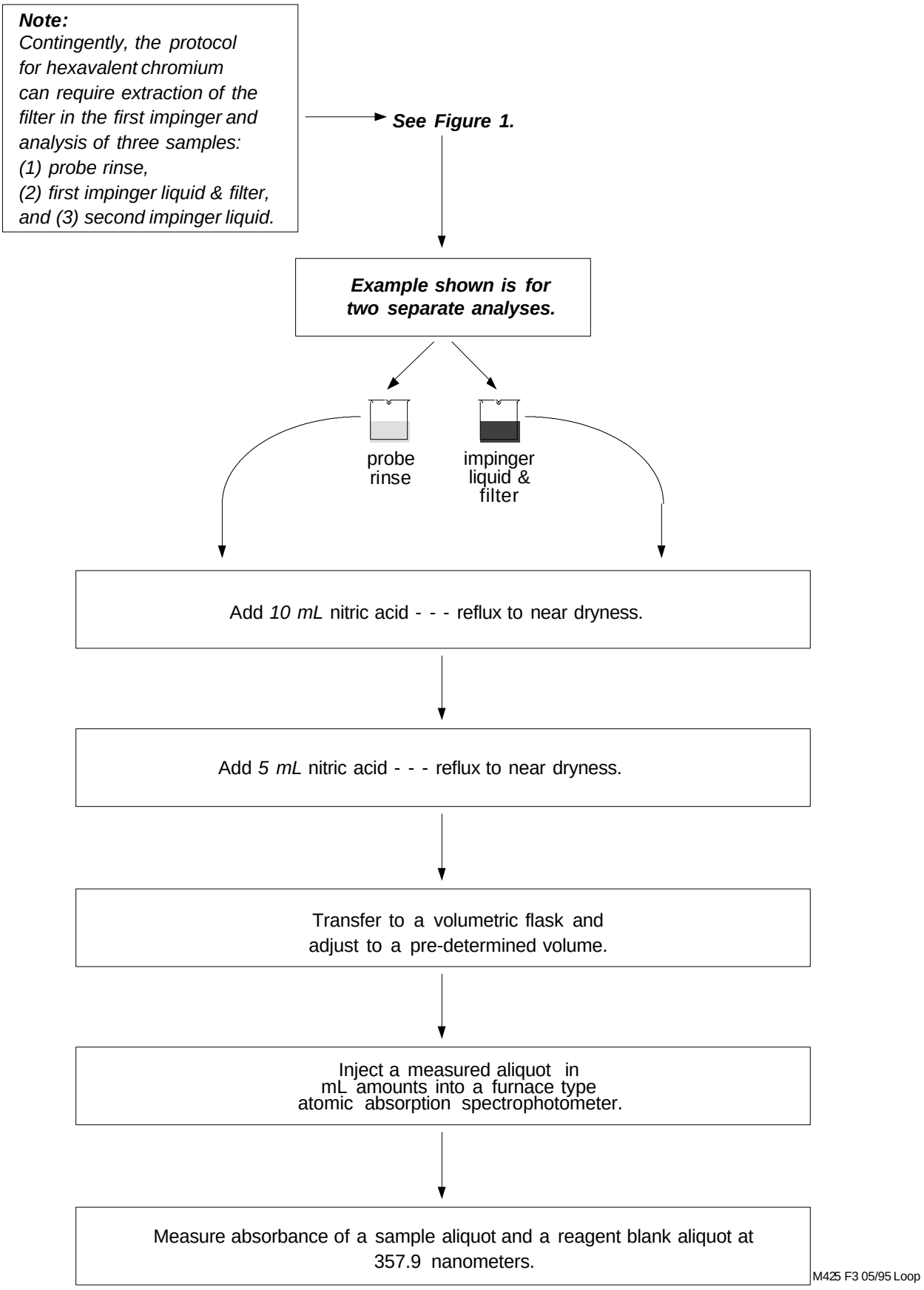
Figure 3.
TOTAL CHROMIUM ANALYSIS



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