



Designation: D7359 – 23

Standard Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)¹

This standard is issued under the fixed designation D7359; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the individual determination of total fluorine, chlorine, and sulfur in aromatic hydrocarbons and their mixtures. Samples containing 0.10 mg/kg to 10 mg/kg of each element can be analyzed.

1.2 This method can be applied to sample concentrations outside the range of the scope by dilution of the sample in an appropriate solvent to bring the total concentrations of fluorine, chlorine, and sulfur within the range covered by the test method. However, it is the responsibility of the analyst to verify the solubility of the sample in the solvent and that the diluted sample results conform to the precision and accuracy of the method.

1.2.1 Special considerations must be made in order to attain detection limits below 1.0 mg/kg in a sample. The instrument must be clean and properly maintained to address potential sources of contamination, or carryover, or both. Multiple sequential injections shall be completed until a stable background is attained. A stable background is considered to be achieved when the analysis of a minimum of three consecutive system blanks have area counts equal to or less than 5 % RSD for the anions of interest.

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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1.5 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. See Section 9.

1.6 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

- D1193 Specification for Reagent Water
- D3437 Practice for Sampling and Handling Liquid Cyclic Products
- D3505 Test Method for Density or Relative Density of Pure Liquid Chemicals
- D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E288 Specification for Laboratory Glass Volumetric Flasks
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E969 Specification for Glass Volumetric (Transfer) Pipets

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

2.2 Other Documents:

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200³

3. Terminology

3.1 Definitions:

3.1.1 *combustion ion chromatography, n*—an analytical system consisting of pyrohydrolytic combustion followed by ion chromatographic detection.

3.1.2 *oxidative pyrohydrolytic combustion, n*—a process in which a sample undergoes combustion at temperatures greater than 900 °C in an oxygen-rich environment and in the presence of excess water vapor not originating from the combustion of the sample. In oxidative pyrohydrolytic combustion, the sample is pyrolyzed into carbon dioxide, water, hydrogen halides, and residual ash; typically elemental oxides.

3.1.3 *halogens (X), n*—the elements fluorine, chlorine, bromine, and iodine.

3.1.4 *hydrogen halide (HX), n*—inorganic compounds with the formula HX where X is one of the halogens: fluorine, chlorine, bromine, and iodine. Hydrogen halides are gases that dissolve in water to give acids.

3.1.5 *sulfur oxide (SO_x), n*—refers to one or more of the following compounds:

3.1.5.1 *sulfur dioxide (SO₂)*

3.1.5.2 *sulfur trioxide (SO₃)*

3.1.5.3 *sulfate (SO₄)*

3.1.6 *system blank, n*—a combustion ion chromatography (CIC) analysis with no solvent or sample injection in which the same combustion, chromatography and time protocols are used as for the sample analysis, but without the combustion of a sample or solvent blank. The system blank must be equal to or less than 50 % (1/2) the area counts of the lowest calibration standard used for calibration and a maximum of 50 % (1/2) of the area count of the solvent blank used in the preparation of the calibration standards for the anions of interest.

3.1.7 *solvent blank, n*—a combustion ion chromatography (CIC) analysis of the solvent used for preparation of the calibration standards in which the same combustion, chromatography, time protocols and injection volumes are used as for the sample analysis. The solvent blank area count must be less than or equal to two times (2×) the system blank and 50 % (1/2) or less than the area counts of the lowest calibration standard used in the calibration of the system for the anions of interest.

3.1.8 *stock standard solution, n*—standard prepared from primary standards and subsequently used to prepare the working standard.

3.1.9 *working standard solution, n*—standard prepared from the stock standard solution and subsequently used to prepare the calibration standards.

3.1.10 *calibration standard, n*—standard prepared from the working standard and subsequently used to calibrate the instrument.

3.2 Abbreviations:

3.2.1 *CIC*—combustion ion chromatography

3.2.2 *Conc*—concentration

3.2.3 *CRM*—certified reference material

3.2.4 *HCl*—hydrogen chloride

3.2.5 *HF*—hydrogen fluoride

3.2.6 *HX*—hydrogen halide

3.2.7 *IC*—ion chromatograph or ion chromatography

3.2.8 *SO_x*—sulfur oxide (SO₂ and SO₃)

3.2.9 *SO₂*—sulfur dioxide

3.2.10 *SO₃*—sulfur trioxide

3.2.11 *SO₄*—sulfate

3.2.12 *SRM*—standard reference material

3.2.13 *Std*—standard

4. Summary of Test Method

4.1 A sample of known weight or volume is placed into a sample boat and introduced at a controlled rate into a high-temperature combustion tube. There the sample is combusted in an oxygen rich pyrohydrolytic environment. The gaseous by-products of the combusted sample are trapped in an absorption medium where the hydrogen halides (HX) formed during combustion disassociate into their respective ions, X⁻ while the sulfur oxides (SO_x) formed are further oxidized to SO₄²⁻ in the presence of an oxidizing agent. An aliquot of known volume of the absorbing solution is then automatically injected into an ion chromatograph (IC) by means of a sample injection valve. The halide and sulfate anions are separated on the anion separation column of the IC. The conductivity of the eluent is reduced with an anion suppression device prior to the ion chromatograph's conductivity detector, where the anions of interest are measured. Quantification of the fluorine, chlorine and sulfur in the original combusted sample is achieved by first calibrating the system with a series of standards containing known amounts of fluorine, chlorine and sulfur and then analyzing unknown samples under the same conditions as the standards. The combined system of pyrohydrolytic combustion followed by ion chromatographic detection is referred to as Combustion Ion Chromatography (CIC).

5. Significance and Use

5.1 The total fluorine, chlorine, and sulfur contained in aromatic hydrocarbon matrices can contribute to emissions, be harmful to many catalytic chemical processes, and lead to corrosion. This test method can be used to determine total sulfur and halogens in aromatic hydrocarbons and their mixtures. The results can be used for compliance determinations when acceptable to a regulatory authority using performance based criteria.

³ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.

6. Interferences

6.1 Substances that co-elute with the anions of interest will interfere. A high concentration of one anion can interfere with other constituents if their retention times are close enough to affect the resolution of their peak.

7. Apparatus

7.1 *Autosampler*, capable of accurately delivering a known volume of sample, typically in the range of 10 μL to 100 μL , into the sample boat.

NOTE 1—The sample syringe should be rinsed with clean solvent followed by a rinse with the next sample when changing from one vial to another. Follow the manufacturer's recommendation to minimize carry-over.

7.2 *Balance*, analytical, with sensitivity to 0.0001 g.

7.3 *Boat Inlet System*—The system provides a sampling port for the introduction of liquid samples into the sample boat and is connected to the inlet of the combustion tube. The system is swept by a humidified inert carrier gas and shall be capable of allowing the quantitative delivery of the material to be analyzed into the oxidation zone at a controlled rate.

7.4 *Boat Inlet Cooler*—Sample volatility requires an apparatus capable of cooling the sample boat prior to sample injection into the boat.

7.5 *Gas Flow Control*—The apparatus must be equipped with flow controllers capable of maintaining a constant flow of oxygen and argon or helium carrier gas.

7.6 *Furnace*—An electric furnace which can maintain a minimum temperature of 900 °C.

7.7 *Gas Absorption Unit*, having an absorption tube with sufficient capacity to hold a minimum of 5 mL which is automatically filled with a known volume of absorption solution by a built-in burette or other similar device. The gas absorption unit is interfaced to the IC and injects an aliquot of the absorption solution into the IC after the sample is combusted and the by-products of combustion are absorbed. The gas absorption unit rinses the absorption tube and the transfer lines from the combustion tube to the gas absorption unit with Type I reagent water (8.2) or other appropriate absorption solution prior to sample combustion and after the absorption solution is injected into the IC to minimize cross contamination.

7.8 *Gas-Tight Sampling Syringe*, of 10 μL , 25 μL , 50 μL , 100 μL , or 250 μL capacity and capable of accurately delivering microliter quantities.

7.9 *Pyrohydrolytic Combustion Tube* made of quartz and capable of withstanding temperatures up to 1100 °C. The combustion tube must be of ample volume and may include quartz wool or other suitable medium to provide sufficient mixing and surface area to ensure complete combustion of the sample.

7.10 *Humidifier Delivery System*, capable of delivering Type I reagent water (8.2) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.

7.11 *Ion Chromatograph (IC)*⁴—An analytical system with all required accessories including columns, suppressor and detector.

7.11.1 *Injection System*, capable of delivering 20 μL to 500 μL with a precision better than 1 % or as recommended for this determination by the manufacturer. Larger volumes can be used as long as the performance criteria of the method are not degraded.

7.11.2 *Pumping System*, capable of delivering mobile phase flows between 0.2 mL/min and 2.5 mL/min with a precision better than 2 %, or as recommended for this determination by the manufacturer.

7.11.3 *Continuous Eluent Generation (optional)*, to automatically prepare and purify the eluent used in the ion chromatography. Electrolytic eluent generation and auto-buret preparation of eluent by means of in-line dilution of a stock solution have been found satisfactory for this method. Other continuous eluent generation devices may be used if the precision and accuracy of the method are not degraded.

7.11.4 *Anion Pre-concentration Column (optional)*, used for anion pre-concentration and matrix elimination. Pre-concentration enables larger volumes of absorbing solution (1 mL to 3 mL) to be analyzed without the associated water dip. Matrix elimination refers to the elimination of any unreacted hydrogen peroxide in the absorbing solution prior to injection onto the guard and anion separator columns and potentially interfere with the fluoride peak resolution.

7.11.5 *Guard Column*, for protection of the analytical column from strongly retained constituents. Improved separation is obtained with additional theoretical plates.

7.11.6 *Anion Separator Column*, capable of producing satisfactory baseline separations of the anion peaks of interest as shown in Fig. 1.

7.11.7 *Anion Suppressor Device*—Reduces the background conductivity of the eluent after separation by the anion separator column. Both chemical and continuous electrolytic suppressors have been found satisfactory for this method. Other anion suppressor devices may be used as long as the precision and accuracy of the method are not degraded.

7.11.8 *Data Acquisition System*—An integrator or computer data handling system capable of integrating the peak areas of an ion chromatograph.

7.12 *Quartz or Ceramic Sample Boats* of sufficient size to hold 10 μL to 100 μL . The boat is filled with quartz wool or other suitable material (8.3) to wick any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, eluent, and regenerator solutions. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the

⁴ Many different companies manufacture automatic ion chromatographs. Consult the specific manufacturer instruction manuals for details regarding setup and operation.

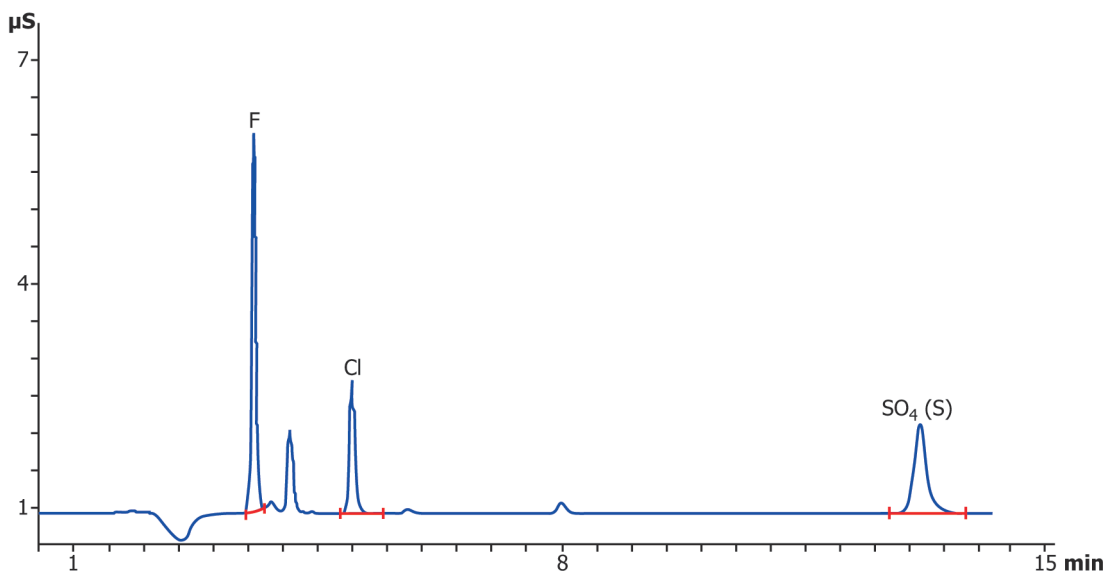


FIG. 1 Anion Peaks of Interest

TABLE 1 Type I Reagent Water Key Specifications

Measurement (unit)	Specification D1193		
	Type I	Type II	Type III
Resistivity (MΩ-cm) at 25 °C	>18	>1	>4
Total organic carbon (ppb)	<50	<50	<200
Sodium (ppb)	<1	<5	<10
Chloride (ppb)	<1	<5	<10
Total silica (ppb)	<3	<3	<500

American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE 2—Purity of reagents are of particular importance when performing trace analysis (samples containing 1 mg/kg or less in analyte concentration). A system reagent blank should provide a chromatographic area response no greater than 50 % (1/2) of the lowest calibration standard.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type 1 having 18 MΩ cm resistance and conforming to Specification D1193. Comply with all ion chromatograph instrument and column vendor requirements for eluent preparation and handling (for example, filtering, degassing, and the like). The reagent water is critical to the performance, repeatability, reproducibility, and accuracy of the method. Therefore, the reagent water used must be of the highest quality available in the lab. A chart of critical specification parameters for Type I reagent water in accordance with Specification D1193 is listed in Table 1.

8.3 *Quartz Wool*, (fine grade) or other suitable absorbent material can be used that is stable and capable of withstanding temperatures inside the furnace.

⁵ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

NOTE 3—Materials meeting the requirements in 8.3 provide a more uniform injection of the sample into the boat by wicking any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace. Consult instrument manufacturer recommendations for further guidance.

8.4 *Argon or Helium*, carrier gas minimum 99.99 % purity.

NOTE 4—Purification scrubbers to ensure the removal of contaminants such as moisture (molecular sieve) and hydrocarbon trap filters (activated charcoal or equivalent) are recommended.

8.5 *Oxygen*, combustion gas minimum 99.75 % purity.

8.6 *Gas Regulators*—Two-stage, gas regulators capable of regulating the pressures to 40 psi to 60 psi must be used for the carrier and combustion gases. Follow instrument manufacturer’s recommendations for pressure regulation.

8.7 *Calibration Standards*—Certified calibration standards from commercial sources or calibration standards prepared in the laboratory containing the elements or anions at the concentrations of interest.

NOTE 5—Other calibration standard sources and diluents may be used if precision and accuracy are not degraded.

NOTE 6—Calibration standards can have a useful shelf life of about three months if properly stored in a cool, dark place.

NOTE 7—A correction for chemical impurity can be used if deemed necessary.

8.8 *Dibenzothiophene*, FW 184.26, 17.40 % S.

8.9 *Fluorobenzoic Acid*, FW 140.11, 13.56 % F or Fluorobenzene, FW 96.10, 19.77% F.

8.10 *2,4,5 Trichlorophenol*, FW 197.46, 53.87 % Cl or Chlorobenzene, FW 112.56, 31.50 % Cl.

8.11 *Hydrogen Peroxide 30 %*, FW 34.01 H₂O₂ (see Section 9 regarding Hazards). Purity must be suitable for trace analysis. It is highly recommended that the concentration of each anion of interest be less than 1 mg/kg.

NOTE 8—Fluka TraceSelect Ultra, Fluka TraceSelect,⁶ and EMD Suprapur⁷ have all proven to work well for this method.

8.12 *Eluent Solution*—Follow the specific guidelines for the preparation and use of the eluent solution from the manufacturer of the columns being used. Other concentrations may be used if precision and accuracy of the method is not degraded. The solutions recommended by the column manufacturer can be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded (see Section 9 regarding Hazards).

8.13 *Suppressor Solutions:*

8.13.1 *Chemical Suppressor Regenerant Solution*—Follow the specific manufacturer guidelines for the preparation and use of the suppressor solution. The manufacturer recommended solutions can be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded.

8.13.2 *Electrolytic Suppressor Current Setting*—Follow the specific guidelines for the current setting from the vendor of the suppressor being used based upon the flow rate and eluent concentration being used for the analysis.

8.14 *Solvent*—The solvent of choice should be capable of dissolving the standard or sample. The solvent should contain less than 0.05 mg/kg of the elements or anions of interest. The blank value must be determined for each new bottle of solvent. Suggested solvents include, but are not limited to, *iso*-octane, xylene, toluene, and methanol.

8.15 *Volumetric Flasks—Type Class A*, in accordance with Specification E288 at the volume required for the preparation of standards, reagents, and solutions.

8.16 *Volumetric Pipets—Type Class A*, in accordance with Specification E969 at the volume required for preparation of standards, reagents, and solutions.

8.17 *Stock Standard Solution(s) of approximately 1000 µg/mL*—Prepare stock standard solution(s) by accurately weighing to within 10 % of the target weights for any or all of the target standard compound(s) listed in 8.17.1 (choose one of the options for Fluorine), 8.17.2 (choose one of the options for Chlorine), and 8.17.3 into a 100 mL Type Class A volumetric flask. Dilute to volume with the selected solvent listed in 8.14. Calculate the actual concentration of the stock standard solution(s) for each element by using the formula in Eq 1 with the actual recorded weight of the target compound used for each element. This stock standard solution can be further diluted to other desired concentrations. Other suitable materials, weights and volumes may be substituted in preparing stock standard solution(s) as long as the performance of the method is not degraded.

NOTE 9—Stock standard solutions from commercial sources can be used if the accuracy, precision, and performance criteria of the method are not degraded.

Target Standard Compound(s)

8.17.1 *Fluorobenzoic Acid, (Fluorine)*, 0.7375 g target weight or Fluorobenzene, (Fluorine), 0.5059 g target weight.

⁶ Fluka TraceSelect Ultra and Fluka TraceSelect are registered trademarks of Sigma-Aldrich Co. LLC.

⁷ EMD Suprapur is a registered trademark of EMD Millipore Corporation.

8.17.2 *2,4,5 Trichlorophenol, (Chlorine)*, 0.1856 g target weight or Chlorobenzene, (Chlorine), 0.3174 g target weight.

8.17.3 *Dibenzothiophene, (Sulfur)*, 0.5748 g target weight.

Calculation of Concentration of Stock Standard Solution

$$\text{Stock Standard Solution}(\mu\text{g/mL}) = (A) (B) (10^6) (P)/(V) (K) \quad (1)$$

where:

- A = weight of the target compound in grams, g,
- B = % concentration of the elements in the respective target compounds listed in 8.8, 8.9, and 8.10,
- V = final diluted volume, mL,
- P = % purity of target standard compounds listed in 8.8, 8.9, and 8.10, and
- K = 100 (correction to convert % to µg/g).

8.18 *Absorbing Solution*—Dilute a sufficient amount of hydrogen peroxide stock solution listed in 8.11 to achieve a final concentration of approximately 100 µg/mL. (Approximately 0.7 mL of 30 % hydrogen peroxide added to 2 L of absorbing solution will give a final concentration of approximately 100 µg/mL.) The use of hydrogen peroxide in the absorbing solution ensures that all SO_x species are converted to SO₄ prior to detection by the IC. Hydrogen peroxide is not required if the measurement of sulfur is not being determined.

NOTE 10—Other concentrations of hydrogen peroxide can be used as long as the performance of the method is met.

NOTE 11—Hydrogen peroxide may not be necessary if the concentration of sulfur in the sample is low since the formation of SO₃ in the absorption solution becomes insignificant. It has been observed that results at concentrations below 5 mg/kg in aromatic compounds typically do not require hydrogen peroxide. If the differences in area counts of the sulfate peak is less than 5 % with and without hydrogen peroxide then one can assume that the use of hydrogen peroxide is not necessary.

NOTE 12—Absorbing solution has a shelf life of one week.

8.19 *Working Standard Solution*—Calculate the correct concentrations obtained from the stock standard solution(s) in 8.17 and prepare a working standard by diluting the stock standard solution(s) with solvent (8.14).

8.19.1 Prepare a 10.0 µg/mL working standard by using a 1.0 mL Type Class A volumetric pipet (Specification E969) and pipet 1.0 mL of the 1000 µg/mL stock standard solution(s) (8.17) into a 100 mL Type Class A volumetric flask (Specification E288) and dilute to mark with solvent.

8.20 *Calibration Standards*—Prepare calibration standards by diluting the working standard solution (8.19.1) to create 0.1 µg/mL, 0.5 µg/mL, 1.0 µg/mL and 5.0 µg/mL calibration standards by pipetting 1.0 mL, 5.0 mL, 10.0 mL, and 50.0 mL of working standard solution with the appropriate Class A volumetric pipets into four separate 100 mL Class A volumetric flasks and dilute to the mark with solvent (8.14). The calibration standards used to calibrate the system will include the solvent (8.14) as zero, the working standard for the 10 µg/mL and encompass the following approximate concentrations: 0.0 µg/mL, 0.1 µg/mL, 0.5 µg/mL, 1.0 µg/mL, 5.0 µg/mL, and 10 µg/mL. The final dilution volumes are determined using the formula in Eq 2.

$$\text{Vol}_{\text{calibration}}(\text{mL}) = \frac{\text{Conc}_{\text{working}} \times \text{Vol}_{\text{working}}}{\text{Conc}_{\text{calibration}}} \quad (2)$$