



Designation: E1600 – 15

Standard Test Methods for Determination of Gold in Cyanide Solutions¹

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1. Scope

1.1 These test methods cover the determination of gold in ore processing cyanide solutions within the following ranges:

Method	Application Range, $\mu\text{g/mL}$
Inductively Coupled Plasma Mass Spectrometry	0.001 to 0.500
Flame Atomic Absorption Spectrometry	0.300 to 10.0

NOTE 1—The lower limit for the Inductively Coupled Plasma Mass Spectrometry Method, 0.001 $\mu\text{g/mL}$, was set following the guidance of Practice E1601. The reproducibility Index, R, was calculated using the total standard deviation for the lowest concentration Youden pair solution.

1.1.1 These test methods may also be applied to cyanide leach solutions from metallurgical evaluation procedures.

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

1.3 The test methods appear in the following order:

Method	Sections
Flame Atomic Absorption Spectrometry	9 – 16
Inductively Coupled Plasma Mass Spectrometry	17 – 24

1.4 *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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautions are given in 11.1, 11.1.1, 11.5, and 12.2.

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

D1293 Test Methods for pH of Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

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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.

D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry

D6888 Test Method for Available Cyanides with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

D7237 Test Method for Free Cyanide and Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)³

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1060 Practice for Interlaboratory Testing of Spectrochemical Methods of Analysis (Withdrawn 1997)³

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology E135.

4. Significance and Use

4.1 In primary metallurgical processes for gold bearing ores, gold is extracted with an alkaline cyanide solution. Metallurgical accounting, process control, and ore evaluation procedures depend on accurate, precise, and prompt measurements of the gold concentrations.

4.2 These test methods are comparative referee methods for compliance with compositional specifications for metal concentration or to monitor processes. It is assumed that all who use these methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is

³ The last approved version of this historical standard is referenced on www.astm.org.

expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide E882, and that proper waste disposal procedures will be followed.

5. Hazards

5.1 For precautions to be observed in these methods, refer to Practice E50.

5.2 Hydrogen cyanide and alkali cyanide are very toxic substances. Use an efficient fume hood. Cyanide must be disposed of with care, avoiding contact with acid that releases hydrogen cyanide gas. Oxidation of cyanide with chlorine or hypochlorite must be carried out at high pH (greater than 11) to prevent generation of toxic cyanogen chloride gas.

5.3 See specific warnings in 11.1.1, 11.5, and 12.2.

6. Sampling and Sample Preparation

6.1 Collect, store, and dispose of the sample in accordance with Practices E50.

6.2 *Preservation*—Determine the pH of the solution immediately after sampling in accordance with Test Method D1293. If the pH of the sample is less than 10, adjust the pH with small additions of solid sodium hydroxide, followed by mixing, until the pH is greater than 10.

6.3 Samples may be preserved to pH 11 or higher if they are also being tested for free and weak acid dissociable cyanide in accordance with Test Methods D6888 or D7237.

6.4 *Test Solutions*—Filter two 50-mL portions of preserved sample solution through a coarse-porosity filter paper.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I or II of Specification D1193. Type III or IV may be used if they effect no measurable change in the blank or sample.

FLAME ATOMIC ABSORPTION SPECTROMETRY

8. Summary of Test Method

8.1 The sample solution is collected and preserved with sodium hydroxide, if necessary, by careful adjustment of pH.

The test solution is filtered and gold content is determined by flame atomic absorption spectrometry.

9. Interferences

9.1 Elements normally found in ore processing cyanide solutions do not interfere. Use of instrumental background correction is required to compensate for nonspecific absorption interferences in the flame.

NOTE 2—Alkaline soluble arsenic can cause low bias on Au by Flame AA. Sample Dilution, matrix spikes, or Method of Standard Additions may be needed.

10. Apparatus

10.1 *Atomic Absorption Spectrometer*, equipped with background correction and capable of measuring gold at the 242.8-nm wavelength using an air and acetylene flame over a linear range from 0.3 µg/mL to 10.0 µg/mL gold.

11. Reagents and Materials

11.1 *Gold Calibration Solutions (0.5, 1.0, 2.0, 5.0, 10.0) µg/mL*—In a fume hood, pipette 10 mL of Gold Standard Solution A (11.2) into a 1-L volumetric flask containing 100 mL of Sodium Cyanide-Sodium Hydroxide Solution (11.5). Dilute to volume and mix (10 µg/mL).

11.1.1 Pipette (5, 10, 20, and 50) mL of the 10 µg/mL gold calibration solution into each of four 100-mL volumetric flasks, respectively. Add 10 mL of Sodium Cyanide-Sodium Hydroxide Solution (11.5), dilute to volume, and mix.

WARNING—Reaction of acid or chlorine and cyanide solutions releases toxic hydrogen cyanide or cyanogen chloride gases. Prepare in a fume hood.

11.2 *Gold Standard Solution A (1 mL – 1.0 µg Au)*—Weigh 1.000 g of gold metal (99.99 % minimum purity) and transfer to a 1-L beaker in a fume hood. Add 200 mL of water, 80 mL of HCl, and 50 mL of HNO₃ (1 + 1). Boil gently to expel NO_x fumes, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

11.2.1 A certified reference solution meeting these specifications may also be used.

NOTE 3—Commercially prepared Gold Cyanide reference solutions should be preserved in NaCN.

11.3 *Reference Solution*—Dilute 100 mL of Sodium Cyanide-Sodium Hydroxide Solution (11.5), to 1 L with water.

11.4 *Sodium Cyanide*.

11.5 *Sodium Cyanide-Sodium Hydroxide Solution*—Dissolve 10 g of sodium hydroxide, then 10 g of sodium cyanide in 1 L of water.

WARNING—The preparation, storage, use, and disposal of sodium cyanide solutions require special care and attention. Avoid any possibility of inhalation, ingestion, or skin contact with the compound, its solution, or its vapors. Work only in a well-ventilated hood.

11.6 *Sodium Hydroxide*.

12. Preparation of Apparatus

12.1 Follow the instrument manufacturer's instructions to adjust the instrument for gold at 242.8 nm. Warm up the

⁴ *Reagent Chemical, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *National Formulary*, U.S. Pharmaceutical Convention, Inc., (USPC), Rockville, MD.

instrument with background correction applied in accordance with the manufacturer's instructions. With the gold hollow cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 242.8-nm line. Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water.

12.2 The use of an air-acetylene, lean, blue flame and caustic stabilized drain bottle is required.

WARNING—Reaction of acid and cyanide solutions in the burner chamber drain bottle may release toxic hydrogen cyanide gas. Add an excess of sodium hydroxide to the drain bottle to maintain the pH above eleven.

12.3 Determine if the instrument precision is acceptable as follows:

12.3.1 Calibrate the instrument in accordance with the manufacturer's instructions in absorbance. Set the absorbance to zero while aspirating the reference solution.

12.3.2 Aspirate the calibration solutions in order of increasing concentration, and select a calibration solution in the absorbance range from 0.2 absorbance units (AU) to 0.4 AU.

12.3.3 Alternate readings on the selected calibration solution and reference solution, and calculate the standard deviation of the readings on the selected calibration solution using accepted statistical methods. Measure the standard deviation in this way at increased measurement integration times until a relatively constant value is achieved.

12.3.4 If the standard deviation under these conditions is greater than 1 % of the average absorbance, determine the cause of the variability (for example, deposits in the burner or clogged capillary), and take corrective action.

12.3.5 If the minimum requirements are not met, do not use the instrument with this test method until the required stability is obtained.

12.3.6 Collect all instrumental measurements for the test method using the instrumental settings which gave the optimum precision of measurement on the selected calibration solution.

12.4 *Linearity of Instrument Response*—Determine if the instrument response is acceptable as follows:

12.4.1 Record absorbance measurements for each of the calibration solutions and the reference solution, prior to determining samples.

12.4.2 Adequate instrument response is obtained if the difference between the 5- $\mu\text{g}/\text{mL}$ calibration solution is sufficient to permit estimation of $1/50$ of the difference between them (0.1 $\mu\text{g}/\text{mL}$).

12.4.3 Adequate linearity is confirmed if the slope of the calibration curve between the 5 $\mu\text{g}/\text{mL}$ and 10 $\mu\text{g}/\text{mL}$ calibration solutions is at least 90 % of the slope between the reference solution and the 0.5- $\mu\text{g}/\text{mL}$ calibration solution.

13. Calibration

13.1 Calibrate the instrument in accordance with the manufacturer's instructions in absorbance or gold concentration.

14. Procedure

14.1 *High-Precision Method*:

14.1.1 Adjust the instrument to zero with the reference solution and measure the test sample solution to determine its place in the order of increasing concentration of the calibration solutions.

14.1.2 Aspirate the test solution and the closely bracketing calibration solutions in order of increasing absorbance or concentration without intervening water aspirations. Repeat three times and calculate the average absorbance or concentration value for each of the three solutions.

14.2 *Linear Curve Method*:

14.2.1 Record the reference solution and calibration solution readings before and after each test sample solution, selecting a different calibration solution after each test solution.

14.2.2 Continue recording measurements until at least three readings have been recorded for all test sample solutions and at least one reading has been recorded for each calibration solution. Calculate the average reading for each of the solutions.

15. Calculation

15.1 *High-Precision Method*—The gold concentration of the test solution is calculated as follows:

$$C_t = \frac{A_t(C_h - C_1)}{(A_h - A_1)} \quad (1)$$

where:

- C_t = concentration of gold in the test solution, $\mu\text{g}/\text{mL}$,
- C_h = concentration of gold in the higher calibration solution, $\mu\text{g}/\text{mL}$,
- C_1 = concentration of gold in the lower calibration solution, $\mu\text{g}/\text{mL}$,
- A_t = average absorbance or concentration reading of the test solution,
- A_h = average absorbance or concentration reading of the higher calibration solution, and
- A_1 = average absorbance or concentration of the lower calibration solution.

15.2 *Linear Curve Method*—Calculate the gold concentration of each test sample solution in micrograms per millilitre using the graphical method, by simple linear regression, or by an equivalent computer method.

15.3 Average the results of the duplicate test sample solutions and round the results to the nearest 0.1 $\mu\text{g}/\text{mL}$ in accordance with Practice E29, unless an alternative rounding method is specified by the customer or applicable material specification.

16. Precision and Bias

16.1 *Precision*—An interlaboratory study was undertaken to test the precision of this test method in accordance with Practice E1060 on six solutions in eight laboratories. The results from the study are summarized in Table 1. Since as few as three laboratories returned results for some of the materials,

TABLE 1 Gold in Cyanide Solutions—Statistical Information

Solutions	Mean, Au, $\mu\text{g/mL}$	R1 (Practice E173), Au, $\mu\text{g/mL}$	R2 (Practice E173), Au, $\mu\text{g/mL}$
1, 4	2.19	0.10	0.18
2, 5	0.19	0.05	0.21
3, 6	0.96	0.02	0.05
7, 10	4.87	0.17	0.22
8, 11	5.97	0.27	0.69
9, 12	10.7	0.15	1.28

Practice E173 was used to estimate the precision. The base data and statistics are documented.⁵

NOTE 4—Solutions 1 through 6 were analyzed by more laboratories than Solutions 7 through 12.

NOTE 5—The reproducibility, R2, of Practice E173 corresponds to the reproducibility index, R, of Practice E1601 and the repeatability, R1, of Practice E173 corresponds to the repeatability index, r, of Practice E1601.

16.1.1 *Repeatability*—The repeatability standard deviation (s_w) ranged from 0.01 $\mu\text{g/mL}$ to 0.12 $\mu\text{g/mL}$ gold over the range of the materials tested. The R1 value in Table 1 for each of the materials tested indicates the maximum difference expected between results in a single laboratory at 95 % confidence.

16.1.2 *Reproducibility*—The reproducibility standard deviation (s_{sr}) ranged from 0.01 $\mu\text{g/mL}$ to 0.15 $\mu\text{g/mL}$ gold over the range of the materials tested. The R2 value in Table 1 for each of the materials tested indicates the maximum difference expected between results in different laboratories at 95 % confidence.

16.2 *Bias*—No information on the bias of this test method is known, because at the time of the interlaboratory study suitable reference materials were not available. The user of this method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

17. Summary of Test Method

17.1 This test method describes the determination of trace gold concentrations by inductively coupled plasma—mass spectrometry (ICP-MS) based on Method D5673. Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by a continuous dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique must be recognized and corrected for (see Section 18 on interferences). Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas,

reagents, or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standardization.

18. Interferences

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

18.1.1 *Abundance Sensitivity*—Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

18.1.2 *Isobaric Polyatomic Ion Interferences*—Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified, and these are listed in Table 2 together with the method element affected. Such interferences must be recognized, and when they cannot be avoided by the selection of an alternative analytical isotope, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

18.1.3 *Physical Interferences*—Physical interferences are associated with the physical processes that govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma—mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (for example, viscosity effects), at the point of aerosol formation and transport to the plasma (for example, surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction, or skimmer cones, or both, reducing the effective diameter of the orifices and, therefore, ion transmission. Dissolved solids levels not exceeding 0.2 % (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards should have similar analytical behavior to the elements being determined.

18.1.4 *Memory Interferences*—Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report: RR:E01-1013.