Designation: D5673 – 16

Standard Test Method for
Elements in Water by Inductively Coupled Plasma—Mass Spectrometry[1]

This standard is issued under the fixed designation D5673; 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 determination of dissolved elements in ground water, surface water, and drinking water. It may also be used for the determination of total-recoverable elements in these waters as well as wastewater.[2]

1.2 This test method should be used by analysts experienced in the use of inductively coupled plasma—mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction.

1.3 It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

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

1.4.1 This method covers the analysis of mine dewatering groundwater and wastewater effluent in the range of 2–120 µg/L dissolved antimony and 3–200 µg/L dissolved arsenic.

1.4.2 This method covers the analysis of metallurgical processing cyanide solutions in the range of 1–500 µg/L dissolved gold.

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

1.6 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods (Withdrawn 2015)[4]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *calibration blank, n*—a volume of water containing the same acid matrix as is in the calibration standards (see 11.1).

3.2.2 *calibration standards, n*—a series of known standard solutions used by the analyst for calibration of the instrument (that is, preparation of the analytical curve) (see Section 11).

3.2.3 *calibration stock solution, n*—a solution prepared from the stock standard solution(s) to verify the instrument response with respect to analyte concentration.

3.2.4 *dissolved, adj*—capable of passing through a 0.45-µm membrane filter.

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] EPA Test Method: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma—Mass Spectrometry, Method 200.8.

[3] 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.

[4] The last approved version of this historical standard is referenced on www.astm.org.

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

TABLE 1 Recommended Analytical Mass and Estimated Instrument Detection Limits

Element	Recommended Analytical Mass	Estimated Instrument Detection Limit, µg/L[A]
Aluminum	27	0.05
Antimony	121	0.08
Arsenic	75	0.9
Barium	137	0.5
Beryllium	9	0.1
Cadmium	111	0.1
Chromium	52	0.07
Cobalt	59	0.03
Copper	63	0.03
Gold	197	0.01
Lead	206, 207, 208	0.08
Manganese	55	0.1
Molybdenum	98	0.1
Nickel	60	0.2
Selenium	82	5.0
Silver	107	0.05
Thallium	205	0.09
Thorium	232	0.03
Uranium	238	0.02
Vanadium	51	0.02
Zinc	66	0.2

[A] Instrument detection limits (3σ) estimated from seven replicate scans of the blank (1 % v/v HNO_3) and three replicate integrations of a multi-element standard.

TABLE 2 Preparation of Metal Stock Solutions [A]

Element or Compound	Weight, g	Solvent
Al	0.1000	10 mL of HCl (sp gr 1.19) + 2 mL of HNO_3 (sp gr 1.42)
Sb	0.1000	0.5 mL of HCl (sp gr 1.19) + 2 mL of HNO_3 (1 + 1)
As_2O_3	0.1320	1 mL of NH_4OH (sp gr 0.902) + 50 mL of H_2O
$BaCO_3$	0.1437	2 mL of HNO_3 (sp gr 1.42) + 10 mL of H_2O
$BeSO_4 \cdot 4H_2O$	1.9650	50 mL of H_2O, add 1 mL of HNO_3 (sp gr 1.42)
Bi_2O_3	0.1115	5 mL of HNO_3 (sp gr 1.42)
Cd	0.1000	5 mL of HNO_3 (1 + 1)
CrO_3	0.1923	1 mL of HNO_3 (sp 1.42) + 10 mL H_2O
Co	0.1000	5 mL of HNO_3 (1 + 1)
Cu	0.1000	5 mL of HNO_3 (1 + 1)
Au	0.1000	20 mL H_2O, ad 8 mL of HCL = 5 mL HNO_3 (1 + 1)
In	0.1000	10 mL of HNO_3 (1 + 1)
$PbNO_3$	0.1599	5 mL of HNO_3 (1 + 1)
MgO	0.1658	10 mL of HNO_3 (1 + 1)
Mn	0.1000	5 mL of HNO_3 (1 + 1)
MoO_3	0.1500	1 mL of NH_4OH (sp gr 0.902) + 10 mL of H_2O
Ni	0.1000	5 mL of HNO_3 (sp gr 1.42)
Sc_2O_3	0.1534	5 mL of HNO_3 (1 + 1)
SeO_2	0.1405	20 mL of H_2O
Ag	0.1000	5 mL of HNO_3 (1 + 1)
Tb_4O_7	0.1176	5 mL of HNO_3 (sp gr 1.42)
$TlNO_3$	0.1303	1 mL of HNO_3 (sp gr 1.42) + 10 mL of H_2O
$Th(NO_3)_4 \cdot 4H_2O$	0.2380	20 mL of H_2O
$UO_2(NO_3)_2 \cdot 6H_2O$	0.2110	20 mL of H_2O
V	0.1000	5 mL of HNO_2 (1 + 1)
Y_2O_3	0.1270	5 mL of HNO_3 (1 + 1)
Zn	0.1000	5 mL of HNO_3 (1 + 1)

[A] Metal stock solutions, 1.00 mL = 1000 µg of metal. Dissolve the listed weights of each metal or compound as specified in Table 2, then dilute to 100 mL with water. The metals may require heat to increase rate of dissolution. Commercially available standards of known purity may be used. Alternate salts or oxides may also be used.

3.2.5 *interference check sample A (ICSA), n*—a solution containing matrix elements at environmental levels that result in interferences on target low level analytes.

3.2.5.1 *Discussion*—ICSA is different from the mixed element standards in 8.5, which are intended for instrument calibration, not for checking interferences. The interferences formed in the ICP can be corrected for by use of element-specific correction equations, collision cell technology with quadrupole-based ICP-MS, or high-resolution ICP-MS.

3.2.6 *interference check sample B (ICSAB), n*—the ICSA solution spiked with 20 µg/L each As and Sb.

3.2.7 *instrumental detection limit (IDL), n*—the concentration equivalent to a signal, that is equal to three times the standard deviation of the blank signal at the selected analytical mass(es).

3.2.8 *internal standard, n*—pure element(s) added in known amount(s) to a solution.

3.2.8.1 *Discussion*—The internal standard is used to measure the instrument response relative to the other analytes that are components of the same solution. The internal standards must be elements that are not a sample component.

3.2.9 *method detection limit (MDL), n*—the minimum analyte concentration that can be identified, measured and reported with 99 % confidence that the analyte concentration is greater than zero.

3.2.9.1 *Discussion*—This confidence level is determined from analysis of a sample in a given matrix containing the analyte(s).

3.2.10 *quality control reference solution (QCS), n*—a solution with the certified concentration(s) of the analytes, prepared by an independent laboratory, and used for a verification of the instrument's calibration.

3.2.11 *reagent blank, n*—a volume of water containing the same matrix as the calibration standards, carried through the entire analytical procedure.

3.2.12 *stock standard solution, n*—a concentrated solution containing one or more analytes, obtained as a certified solution from a reputable source or prepared as described in Table 2.

3.2.13 *total-recoverable, adj*—determinable by the digestion method included in this procedure (see 12.2).

3.2.14 *tuning solution, n*—a solution that is used to determine acceptable instrument performance prior to calibration and sample analysis.

3.3 *Acronyms:*
3.3.1 *ICSA, n*—interference check sample A
3.3.2 *ICSAB, n*—interference check sample B
3.3.3 *IDL, n*—instrumental detection limit
3.3.4 *MDL, n*—method detection limit
3.3.5 *QCS, n*—quality-control reference solution

4. Summary of Test Method

4.1 This test method describes the multi-element determination of trace elements by inductively coupled plasma—mass spectrometry (ICP-MS). 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 6 on interferences). Such corrections must include compensation for isobaric elemental interferences and interferences from poly-atomic ions derived from the plasma gas, reagents, or sample matrix. Instrumental drift as well as suppressions or enhance-ments of instrument response caused by the sample matrix must be corrected for by the use of internal standardization.

5. Significance and Use

5.1 The test method is useful for the determination of element concentrations in many natural waters, metallurgical process cyanide solutions and wastewaters. It has the capability for the determination of up to 21 elements. High analysis sensitivity can be achieved for some elements that are difficult to determine by other techniques.

6. Interferences

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

6.1.1 *Isobaric Elemental Interferences*—Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use by ICP-MS. All elements determined by this test method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this test method (see Table 3), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical iso-topes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calcula-tions. Relevant isotope ratios and instrument bias factors should be established prior to the application of any correc-tions.

6.1.2 *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.

6.1.3 *Isobaric Polyatomic Ion Interferences*—Isobaric poly-atomic 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 4 together with the method elements 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.

6.1.4 *Physical Interferences*—Physical interferences are as-sociated 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 deter-mined.

TABLE 3 Recommended Analytical Isotopes and Additional Masses That Are Recommended To Be Monitored

Isotope[A]	Element of Interest
27	Aluminum
121, 123	Antimony
75	Arsenic
135, 137	Barium
9	Beryllium
106, 108, 111, 114	Cadmium
52, 53	Chromium
59	Cobalt
63, 65	Copper
206, 207, 208	Lead
55	Manganese
95, 97,98	Molybdenum
60, 62	Nickel
77, 82	Selenium
107, 109	Silver
203, 205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66, 67, 68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

[A] Isotopes recommended for analytical determination are underlined. These masses were recommended and are reflected in the precision and bias data. Alternate masses may be used but interferences must be documented.