



Designation: D5673 – 10

Standard Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry¹

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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.

1.5 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.*

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.

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

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, 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 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, n*—those elements that will pass through a 0.45-µm membrane filter.

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.

*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
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

^AInstrument detection limits (3σ) estimated from seven replicate scans of the blank (1 % v/v HNO₃) and three replicate integrations of a multi-element standard.

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

3.2.5.1 *Discussion*—The interferences formed in the ICP can be corrected for by use of element-specific correction equations or collision cell technology with quadrupole-based ICP-MS, or high resolution ICP-MS.

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

3.2.7 *instrumental detection limit (IDL)*, *n*—the concentration equivalent to a signal, which 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 analyte(s) added in known amount(s) to a solution.

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

3.2.9 *method detection limit (MDL)*, *n*—the minimum concentration of an analyte 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 *total-recoverable*, *n*—a term relating to forms of each element that are determinable by the digestion method included in this procedure (see 12.2).

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

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 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.

5. Significance and Use

5.1 The test method is useful for the determination of element concentrations in many natural waters and wastewaters. It has the capability for the determination of up to 20 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. 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 2), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes 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

TABLE 2 Recommended Analytical Isotopes and Additional Masses That Are Recommended To Be Monitored

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

^AIsotopes 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.

isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

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 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 3** 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 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

TABLE 3 Common Molecular Ion Interferences

Background Molecular Ions		
Molecular Ion	Mass	Element Interference ^A
NH ⁺	15	...
OH ⁺	17	...
OH ₂ ⁺	18	...
C ₂ ⁺	24	...
CN ⁺	26	...
CO ⁺	28	...
N ₂ ⁺	28	...
N ₂ H ⁺	29	...
NO ⁺	30	...
NOH ⁺	31	...
O ₂ ⁺	32	...
O ₂ H ⁺	33	...
³⁶ ArH ⁺	37	...
³⁶ ArH ⁺	39	...
⁴⁰ ArH ⁺	41	...
CO ₂ ⁺	44	...
CO ₂ H ⁺	45	Sc
ArC ⁺ , ArO ⁺	52	Cr
ArN ⁺	54	Cr
ArNH ⁺	55	Mn
ArO ⁺	56	...
ArOH ⁺	57	...
⁴⁰ Ar ³⁶ Ar ⁺	76	Se
⁴⁰ Ar ³⁸ Ar ⁺	78	Se
⁴⁰ Ar ₂ ⁺	80	Se
Matrix Molecular Ions		
Chloride		
³⁵ ClO ⁺	51	V
³⁵ ClOH ⁺	52	Cr
³⁷ ClO ⁺	53	Cr
³⁷ ClOH ⁺	54	Cr
Ar ³⁵ Cl ⁺	75	As
Ar ³⁷ Cl ⁺	77	Se
Sulphate		
³² SO ⁺	48	...
³² SOH ⁺	49	...
³⁴ SO ⁺	50	V, Cr
³⁴ SOH ⁺	51	V
SO ₂ ⁺ , S ₂ ⁺	64	Zn
Ar ³² S ⁺	72	...
Ar ³⁴ S ⁺	74	...
Phosphate		
PO ⁺	47	...
POH ⁺	48	...
PO ₂ ⁺	63	Cu
ArP ⁺	71	...
Group I, II Metals		
ArNa ⁺	63	Cu
ArK ⁺	79	...
ArCa ⁺	80	...
Matrix Oxides ^B		
TiO	62 to 66	Ni, Cu, Zn
ZrO	106 to 112	Ag, Cd
MoO	108 to 116	Cd

^AMethod elements or internal standards affected by molecular ions.

^BOxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored if samples are likely to contain high levels of these elements. Mo is monitored as a method analyte.

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.