ASTM

Designation: D 5673 – 96

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

This standard is issued under the fixed designation D 5673; 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.

1.5 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[3]

D 1129 Terminology of Terms Relating to Water[3]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]

D 1193 Specification for Reagent Water

D 3370 Practices for Sampling Water from Closed Conduits[3]

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D 1129.

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

[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.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

3.2.3 *calibration standards*—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).

3.2.4 *dissolved*—those elements that will pass through a 0.45-µm membrane filter.

3.2.5 *instrumental detection limit*—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).

3.2.6 *internal standard*—pure analyte(s) added in known amount(s) to a solution. 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.

3.2.7 *method detection limit*—the minimum concentration of an analyte that can be identified, measured and reported with 99 % confidence that the analyte concentration is greater than zero. This confidence level is determined from analysis of a

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[1] This test method is under the jurisdiction of ASTM Committee D-19 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] *Annual Book of ASTM Standards*, Vol 11.01.

sample in a given matrix containing the analyte(s).

3.2.8 *quality control reference solution*—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.

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

3.2.10 *total-recoverable*—a term relating to forms of each element that are determinable by the digestion method included in this procedure (see 12.2).

3.2.11 *tuning solution*—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 7 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.

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
135, <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, 207, 208</u>	Lead
<u>55</u>	Manganese
95, 97,<u>98</u>	Molybdenum
<u>60</u>, 62	Nickel
77, <u>82</u>	Selenium
<u>107</u>, 109	Silver
203, <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

[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.

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 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.

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_2H^+	29	...
NO^+	30	...
NOH^+	31	...
O_2^+	32	...
O_2H^+	33	...
$^{36}ArH^+$	37	...
$^{36}ArH^+$	39	...
$^{40}ArH^+$	41	...
CO_2^+	44	...
CO_2H^+	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

[A] Method elements or internal standards affected by molecular ions.

[B] Oxide 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.

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 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.

6.1.5 *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 torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank consisting of HNO_3(1+49) in water between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the method detection limit should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be re-analyzed after a long rinse period.

7. Apparatus

7.1 *Inductively Coupled Plasma–Mass Spectrometer*—Instrument capable of scanning the mass range 5 to 250 amu with a minimum resolution capability of 1 amu peak width at 5 % peak height. Instrument may be fitted with a conventional or extended dynamic range detection system. See manufacturers instruction manual for installation and operation.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that reagents shall conform to the specifications of the committee on analytical reagents of the American Chemical Society, [4]

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[4] *Reagent Chemicals, American Chemical Society Specifications*, 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.