



Designation: D5673 – 16

# Standard Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry<sup>1</sup>

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 ( $\epsilon$ ) 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.<sup>2</sup>

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  $\mu\text{g/L}$  dissolved antimony and 3–200  $\mu\text{g/L}$  dissolved arsenic.

1.4.2 This method covers the analysis of metallurgical processing cyanide solutions in the range of 1–500  $\mu\text{g/L}$  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.*

<sup>1</sup> 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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<sup>2</sup> 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:<sup>3</sup>

- 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)<sup>4</sup>

## 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- $\mu\text{m}$  membrane filter.

<sup>3</sup> 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.

<sup>4</sup> The last approved version of this historical standard is referenced on www.astm.org.

\*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, $\mu\text{g/L}^A$
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

<sup>A</sup> Instrument detection limits ( $3\sigma$ ) estimated from seven replicate scans of the blank (1 % v/v  $\text{HNO}_3$ ) and three replicate integrations of a multi-element standard.

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  $\mu\text{g/L}$  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.

**TABLE 2 Preparation of Metal Stock Solutions<sup>A</sup>**

Element or Compound	Weight, g	Solvent
Al	0.1000	10 mL of HCl (sp gr 1.19) + 2 mL of $\text{HNO}_3$ (sp gr 1.42)
Sb	0.1000	0.5 mL of HCl (sp gr 1.19) + 2 mL of $\text{HNO}_3$ (1 + 1)
$\text{As}_2\text{O}_3$	0.1320	1 mL of $\text{NH}_4\text{OH}$ (sp gr 0.902) + 50 mL of $\text{H}_2\text{O}$
$\text{BaCO}_3$	0.1437	2 mL of $\text{HNO}_3$ (sp gr 1.42) + 10 mL of $\text{H}_2\text{O}$
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$	1.9650	50 mL of $\text{H}_2\text{O}$ , add 1 mL of $\text{HNO}_3$ (sp gr 1.42)
$\text{Bi}_2\text{O}_3$	0.1115	5 mL of $\text{HNO}_3$ (sp gr 1.42)
Cd	0.1000	5 mL of $\text{HNO}_3$ (1 + 1)
$\text{CrO}_3$	0.1923	1 mL of $\text{HNO}_3$ (sp 1.42) + 10 mL $\text{H}_2\text{O}$
Co	0.1000	5 mL of $\text{HNO}_3$ (1 + 1)
Cu	0.1000	5 mL of $\text{HNO}_3$ (1 + 1)
Au	0.1000	20 mL $\text{H}_2\text{O}$ , ad 8 mL of HCL = 5 mL $\text{HNO}_3$ (1 + 1)
In	0.1000	10 mL of $\text{HNO}_3$ (1 + 1)
$\text{PbNO}_3$	0.1599	5 mL of $\text{HNO}_3$ (1 + 1)
MgO	0.1658	10 mL of $\text{HNO}_3$ (1 + 1)
Mn	0.1000	5 mL of $\text{HNO}_3$ (1 + 1)
$\text{MoO}_3$	0.1500	1 mL of $\text{NH}_4\text{OH}$ (sp gr 0.902) + 10 mL of $\text{H}_2\text{O}$
Ni	0.1000	5 mL of $\text{HNO}_3$ (sp gr 1.42)
$\text{Sc}_2\text{O}_3$	0.1534	5 mL of $\text{HNO}_3$ (1 + 1)
$\text{SeO}_2$	0.1405	20 mL of $\text{H}_2\text{O}$
Ag	0.1000	5 mL of $\text{HNO}_3$ (1 + 1)
$\text{Tb}_4\text{O}_7$	0.1176	5 mL of $\text{HNO}_3$ (sp gr 1.42)
$\text{TlNO}_3$	0.1303	1 mL of $\text{HNO}_3$ (sp gr 1.42) + 10 mL of $\text{H}_2\text{O}$
$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$	0.2380	20 mL of $\text{H}_2\text{O}$
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.2110	20 mL of $\text{H}_2\text{O}$
V	0.1000	5 mL of $\text{HNO}_2$ (1 + 1)
$\text{Y}_2\text{O}_3$	0.1270	5 mL of $\text{HNO}_3$ (1 + 1)
Zn	0.1000	5 mL of $\text{HNO}_3$ (1 + 1)

<sup>A</sup> Metal stock solutions, 1.00 mL = 1000  $\mu\text{g}$  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.

3.2.11 *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 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, 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 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 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

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

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

<sup>A</sup> 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.

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 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.

**TABLE 4 Common Molecular Ion Interferences**

Background Molecular Ions		
Molecular Ion	Mass	Element Interference <sup>A</sup>
NH <sup>+</sup>	15	...
OH <sup>+</sup>	17	...
OH <sub>2</sub> <sup>+</sup>	18	...
C <sub>2</sub> <sup>+</sup>	24	...
CN <sup>+</sup>	26	...
CO <sup>+</sup>	28	...
N <sub>2</sub> <sup>+</sup>	28	...
N <sub>2</sub> H <sup>+</sup>	29	...
NO <sup>+</sup>	30	...
NOH <sup>+</sup>	31	...
O <sub>2</sub> <sup>+</sup>	32	...
O <sub>2</sub> H <sup>+</sup>	33	...
<sup>36</sup> ArH <sup>+</sup>	37	...
<sup>36</sup> ArH <sup>+</sup>	39	...
<sup>40</sup> ArH <sup>+</sup>	41	...
CO <sub>2</sub> <sup>+</sup>	44	...
CO <sub>2</sub> H <sup>+</sup>	45	Sc
ArC <sup>+</sup> , ArO <sup>+</sup>	52	Cr
ArN <sup>+</sup>	54	Cr
ArNH <sup>+</sup>	55	Mn
ArO <sup>+</sup>	56	...
ArOH <sup>+</sup>	57	...
<sup>40</sup> Ar <sup>36</sup> Ar <sup>+</sup>	76	Se
<sup>40</sup> Ar <sup>38</sup> Ar <sup>+</sup>	78	Se
<sup>40</sup> Ar <sub>2</sub> <sup>+</sup>	80	Se
<sup>118</sup> Ta <sup>16</sup> O <sup>+</sup>	197	Au
Matrix Molecular Ions		
Chloride		
<sup>35</sup> ClO <sup>+</sup>	51	V
<sup>35</sup> ClOH <sup>+</sup>	52	Cr
<sup>37</sup> ClO <sup>+</sup>	53	Cr
<sup>37</sup> ClOH <sup>+</sup>	54	Cr
Ar <sup>35</sup> Cl <sup>+</sup>	75	As
Ar <sup>37</sup> Cl <sup>+</sup>	77	Se
Sulphate		
<sup>32</sup> SO <sup>+</sup>	48	...
<sup>32</sup> SOH <sup>+</sup>	49	...
<sup>34</sup> SO <sup>+</sup>	50	V, Cr
<sup>34</sup> SOH <sup>+</sup>	51	V
SO <sub>2</sub> <sup>+</sup> , S <sub>2</sub> <sup>+</sup>	64	Zn
Ar <sup>32</sup> S <sup>+</sup>	72	...
Ar <sup>34</sup> S <sup>+</sup>	74	...
Phosphate		
PO <sup>+</sup>	47	...
POH <sup>+</sup>	48	...
PO <sub>2</sub> <sup>+</sup>	63	Cu
ArP <sup>+</sup>	71	...
Group I, II Metals		
ArNa <sup>+</sup>	63	Cu
ArK <sup>+</sup>	79	...
ArCa <sup>+</sup>	80	...
Matrix Oxides <sup>B</sup>		
TiO	62 to 66	Ni, Cu, Zn
ZrO	106 to 112	Ag, Cd
MoO	108 to 116	Cd

<sup>A</sup> Method elements or internal standards affected by molecular ions.

<sup>B</sup> 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.

6.1.5 *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<sub>3</sub> (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 *Block Digester, Hot Plate or Steam Bath*—Suitable for reducing acidified sample volume from 103 mL to less than 25 mL.

7.1.1 Block digester systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block.

7.2 *Block Digester Tubes, 125-mL capacity*—For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

7.3 *Inductively Coupled Plasma–Mass Spectrometer*—Instrument capable of measuring 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.

7.4 *Membrane Filter Assembly*—A borosilicate glass, stainless steel, or plastic funnel with a flat, fritted, or grid base so as to provide uniform support and filterable surface. The top section of the funnel shall fit over the edge of the filter to provide a seal. The top should be removable to allow easy access for removing the filter. A Gooch crucible with a fritted bottom may be used in lieu of the funnel.

## 8. Reagents and Materials

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

**TABLE 5 Internal Standards and Limitations of Use**

Internal Standard	Mass	Possible Limitation
Lithium	6	May be present in samples
Scandium <sup>A</sup>	45	Polyatomic ion interference
Yttrium <sup>A</sup>	89	May be present in samples
Rhodium	103	...
Indium <sup>A</sup>	115	Isobaric interference by Sn
Terbium <sup>A</sup>	159	...
Holmium	165	...
Lutetium	175	...
Platinum	195	May be present in samples
Bismuth <sup>A</sup>	209	May be present in samples

<sup>A</sup> Internal standards recommended for use with this test method. It is also recommended when analyzing a new sample matrix that a scan for the presence of internal standards be performed.

on analytical reagents of the American Chemical Society,<sup>5</sup> where such specifications are available. The high sensitivity of inductively coupled plasma—mass spectrometry may require reagents of higher purity. Stock standard solutions are prepared from high-purity metals, oxides, or non-hygroscopic reagent grade salts using Type I, II, or III reagent water and ultrapure acids.

**8.2 Purity of Water**—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to ASTM Type I water (Specification **D1193**). Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method.

**8.3 Ammonium Hydroxide** (sp gr 0.902)—Concentrated ammonium hydroxide (NH<sub>4</sub>OH), ultrapure or equivalent.

**8.4 Argon**—High purity grade (99.99 %).

**8.5 Filter Membranes**—Acid washed or high purity, so that metal content does not contribute significantly to the reagent blank, 0.45 μm porosity.

**8.6 Hydrochloric Acid** (sp gr 1.19)—Concentrated hydrochloric acid (HCl), ultrapure or equivalent.

**8.7 Hydrochloric Acid** (1+1)—Add one volume of hydrochloric acid (sp gr 1.19) to 1 volume of water.

**8.8 Internal Standards**—Internal standards are recommended in all analyses to correct for instrument drift and physical interferences. A list of acceptable internal standards is provided in **Table 5**. For full mass range scans use a minimum of three internal standards with the use of five suggested. Add internal standards to blanks, samples and standards in a like manner. A concentration of 100 μg/L of each internal standard is recommended.

**8.9 Mixed and Single Standard Solutions**—Prepare mixed standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see **Note 1**). Prior to preparing mixed standard solutions, each stock solution needs

<sup>5</sup> *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

to be analyzed separately to determine possible interferences on the other analytes or the presence of impurities. Care needs to be taken when preparing the mixed standard solutions to ensure that the elements are compatible and stable.

**NOTE 1**—Mixed calibration standards will vary, depending on the number of elements being determined. Commercially prepared mixed calibration standards of appropriate quality may be used. An example of mixed calibration standards for 20 elements is as follows:

Mixed Standard Solution I		Mixed Standard Solution II
Aluminum	Manganese	Barium
Antimony	Molybdenum	Silver
Arsenic	Nickel	
Beryllium	Selenium	
Cadmium	Thallium	
Chromium	Thorium	
Cobalt	Uranium	
Copper	Vanadium	
Lead	Zinc	

Prepare multi-element mixed standard solutions I and II (1 mL = 10 μg) by pipetting 1.00 mL of each single element stock solution (see **Table 2**) onto a 100 mL volumetric flask and any internal standards. Add 50 mL of HNO<sub>3</sub> (1+99) and dilute to 100 mL with HNO<sub>3</sub> (1 + 99). The ICSA, which is used as an interference check, is different from the mixed element standards, which are used for instrument calibration.

**8.10 Nitric Acid** (sp gr 1.42)—Concentrated nitric acid (HNO<sub>3</sub>), ultrapure or equivalent.

**8.11 Nitric Acid** (1+1)—Add one volume of nitric acid (sp gr 1.42) to 1 volume of water.

**8.12 Nitric Acid** (1+49)—Add one volume of nitric acid (sp gr 1.42) to 49 volumes of water.

**8.13 Nitric Acid** (1+99)—Add one volume of nitric acid (sp gr 1.42) to 99 volumes of water.

**8.14 Stock Solutions**—Preparation procedures for stock solutions of each element are listed in **Table 2**.

**8.15 Reagent Blank**—This solution must contain all the reagents and be the same volume as used in the processing of the samples and any internal standards. Carry reagent blank through the complete procedure. Reagent blank must contain the same acid concentration in the final solution as the sample solution used for analysis.

**8.16 Stock Solutions**—Preparation procedures for stock solutions of each element are listed in **Table 2**.

## 9. Hazards

9.1 The toxicity or carcinogenicity of each reagent used in this test method has not been precisely defined; however, each chemical should be treated as a potential health hazard. Adequate precautions should be taken to minimize exposure of personnel to chemicals used in this test method.

## 10. Sampling

10.1 Collect the samples in accordance with the applicable standards, Practice **D1066** or Practices **D3370**.

10.2 If only dissolved elements are to be determined, filter the sample through a 0.45-μm membrane filter before acidification (see **Note 2**). Preserve the samples at the time of collection by immediately adding nitric acid (sp gr 1.42) to

adjust the pH to 2. Normally, 2 mL of HNO<sub>3</sub> (sp gr 1.42) is required per litre of sample.

10.2.1 Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. This could reduce hazards of working with acids in the field when appropriate, particularly with samples containing cyanide. If cyanide is present in the solution matrix, perform acidification in a fume hood. If nitric acid addition results in formation of precipitates, proceed with the total-recoverable digestion procedure (12.2). Solutions are ready for analysis after sample preparation is complete.

NOTE 2—Depending on the manufacturer, some filters have been found to be contaminated to various degrees with heavy metals. Care should be exercised in selecting a source of these filters. A good practice is to wash the filters first with HNO<sub>3</sub> (1+99) and then with 50 mL of the sample before filtering.

### 11. Calibration and Standardization

11.1 Calibrate the instrument for the elements chosen over a suitable concentration range by atomizing the calibration blank and mixed standard solutions, including any internal standards, and recording their concentrations and signal intensities. It is recommended that a minimum of three standards and a blank be used for calibration with one of the standards at three to five times the elements' MDL. It is recommended that the calibration blank and standards be matrix matched with the same acid concentration contained in the samples. Analyze appropriate reference solutions to validate the calibration of the instrument before proceeding to the sample analysis.

11.2 Alternatively, calibrate according to the manufacturer's instructions if equivalent results are achieved.

### 12. Procedure

12.1 To determine dissolved elements, add 1 mL of concentrated HNO<sub>3</sub> (sp gr 1.42) to 100 mL of filtered, acid-preserved sample and any internal standards. Proceed with 12.3 for all elements except for gold in a cyanide matrix, for gold in the sodium hydroxide preserved matrix proceed at 12.2 in a fume hood.

12.2 When determining total-recoverable elements, use 100 mL of a well mixed, acid-preserved sample appropriate for the expected level of elements containing not more than 0.25 % (w/v) total solids.

12.2.1 Transfer the sample to a 125 mL (or larger) beaker, digestion tube, or flask and add any internal standards, 2 mL of HNO<sub>3</sub> (1+1) and 1 mL HCl (1+1) and heat on a block digester, steam bath, or hot plate until the volume has been reduced to near 25 mL, making certain the sample does not boil. Cool the sample, and if necessary, filter or let insoluble material settle to avoid clogging of the nebulizer. Adjust to original sample volume of 100 mL, in a volumetric flask. To determine total-recoverable elements, proceed with 12.3. This method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains <0.1 mg/L silver.

NOTE 3—Many laboratories have found block digestion systems a

TABLE 6 Recommended Elemental Equations for Data Calculation

Element	Elemental Equation <sup>A</sup>	Note
Al	(1.000) ( <sup>27</sup> C)	...
Sb	(1.000) ( <sup>121</sup> C)	...
As	(1.000) ( <sup>75</sup> C) – (3.127) [( <sup>77</sup> C) – (0.815) ( <sup>82</sup> C)]	B
Ba	(1.000) ( <sup>137</sup> C)	...
Be	(1.000) ( <sup>9</sup> C)	...
Cd	(1.000) ( <sup>111</sup> C) – (1.073) [( <sup>108</sup> C) – (0.712) ( <sup>106</sup> C)]	D
Cr	(1.000) ( <sup>52</sup> C)	...
Co	(1.000) ( <sup>59</sup> C)	...
Cu	(1.000) ( <sup>63</sup> C)	...
Au	(1.000) ( <sup>197</sup> C)	...
Pb	(1.000) ( <sup>206</sup> C) + (1.000) ( <sup>207</sup> C) + (1.000) ( <sup>208</sup> C)	E
Mn	(1.000) ( <sup>55</sup> C)	...
Mo	(1.000) ( <sup>98</sup> C) – (0.146) ( <sup>99</sup> C)	F
Ni	(1.000) ( <sup>60</sup> C)	...
Se	(1.000) ( <sup>82</sup> C)	G
Ag	(1.000) ( <sup>107</sup> C)	...
Tl	(1.000) ( <sup>205</sup> C)	...
Th	(1.000) ( <sup>232</sup> C)	...
U	(1.000) ( <sup>238</sup> C)	...
V	(1.000) ( <sup>51</sup> C) – (3.127) [( <sup>53</sup> C) – (0.113) ( <sup>52</sup> C)]	H
Zn	(1.000) ( <sup>66</sup> C)	...
Kr	(1.000) ( <sup>83</sup> C)	...
Pd	(1.000) ( <sup>105</sup> C)	...
Ru	(1.000) ( <sup>99</sup> C)	...
Sn	(1.000) ( <sup>118</sup> C)	...
Bi	(1.000) ( <sup>209</sup> C)	I
In	(1.000) ( <sup>115</sup> C) – (0.016) ( <sup>118</sup> C)	J
Sc	(1.0000) ( <sup>45</sup> C)	K
Tb	(1.000) ( <sup>159</sup> C)	...
Y	(1.000) ( <sup>89</sup> C)	I

<sup>A</sup> C = calibration blank subtracted counts at specified mass.  
<sup>B</sup> Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.  
<sup>C</sup> Correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.  
<sup>D</sup> In 0.4 % v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.  
<sup>E</sup> Allowance for isotopic variability of lead isotopes.  
<sup>F</sup> Isobaric elemental correction for ruthenium.  
<sup>G</sup> Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.  
<sup>H</sup> Correction for chloride interference with adjustment for Cr53. ClO 51/53 ratio may be determined from the reagent blank.  
<sup>I</sup> May be present in environmental samples.  
<sup>J</sup> Isobaric elemental correction for tin.  
<sup>K</sup> Polyatomic ion interference.

useful way to digest samples for trace metals analysis.

NOTE 4—Internal standards may be added after digestion, treating samples and standards alike, instead of before digestion.

12.3 Atomize each solution and record signal's intensity or calculated concentration for each mass of interest. Atomize a rinse blank consisting of HNO<sub>3</sub> (1+49) in water between samples.

12.4 Minimum quality control requirements for this method include (see Section 15):

12.4.1 Monitoring of internal standard area counts in each sample,

12.4.2 Analysis of one reagent blank with each set of samples as continuing check on sample contamination,

12.4.3 An interference check sample containing 300-mg/L calcium and 2000-mg/L chloride shall be included.

12.4.3.1 Analysis of ICSA containing 300 mg/L of calcium and 2000 mg/L of chloride prior to analysis of mine dewatering