D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

9.10.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

9.11 If less than acceptable accuracy and precision data are generated, additional quality control tests (Secs. 9.11.1 and 9.11.2) are recommended prior to reporting concentration data for the elements in this method. At a minimum these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These test will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

9.11.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.11.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.11.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

9.12 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with proper operating parameters established as detailed below. The instrument should be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operating conditions, the analyst should follow the instructions provided by the instrument manufacturer.

10.2 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.

10.2.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of the appropriate correction equations or other routines for correcting spectral interferences. These data should be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data should be kept on file and be available for review by the data user or auditor.

10.2.2 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference corrections need to be established for each individual target analyte on each particular instrument. All measurements (both target analytes and constituents which interfere with the target analytes) need to be within the instrument linear range where the correction equations are valid.

10.2.3 The lower limits of quantitation should be established for all isotope masses utilized for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

10.2.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

10.2.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix-specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

10.2.4 Specific recommended isotopes for the analytes noted in Sec. 1.2 are provided in Table 2. Other isotopes may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of mass spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task.

10.3 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 2.

10.4 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions (Sec. 7.5), the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument standardization by analyzing appropriate QC samples as follows.

10.4.1 Individual or mixed calibration standards should be prepared from known primary stock standards every six months to one year as needed based on the concentration stability as confirmed from the ICV analyses. The analysis of the ICV, which is prepared from a source independent of the calibration standards, is necessary to verify the instrument performance once the system has been calibrated for the desired target analytes. It is recommended that the ICV solution be obtained commercially as a certified traceable reference material such that an expiration date can be assigned. Alternately, the ICV solution can be prepared from an independent source on an as needed basis depending on the ability to meet the calibration verification criteria. If the ICV analysis is outside of the acceptance criteria, at a minimum the calibration standards must be prepared fresh and the instrument recalibrated prior to beginning sample analyses. Consideration should also be given to preparing fresh ICV standards if the new calibration cannot be verified using the existing ICV standard.

NOTE: This method describes the use of both a low-level and mid-level ICV standard analysis. For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.

10.4.1.1 The calibration standards should be prepared using the same type of acid or combination of acids and at similar concentrations as will result in the samples following processing.

10.4.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation for each desired target analyte. Additionally, if the calibration blank response or continuing calibration blank verification is used to calculate a theoretical concentration, this value should be less than the level of acceptable blank contamination as specified in the approved quality assurance project planning documents. If this is not the case, the reason for the out-of-control condition must be found and corrected, and the sample analyses may not proceed or the previous ten samples need to be reanalyzed.

10.4.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards as noted in Sec. 7.5. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. Flush the system with the rinse blank (Sec. 7.6.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards as outlined in Sec. 10.4.3.

Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards that effectively bracket the desired sample concentration range. If low-level as compared to mid- or high-level sample concentrations are expected, the calibration standards should be prepared at the appropriate concentrations in order to demonstrate the instrument linearity within the anticipated

sample concentration range. For all multi-point calibration scenarios, the lowest non-zero standard concentration should be considered the lower limit of quantitation.

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. See Sec. 10.4.4 for recommendations on how to determine the linear dynamic range, while the guidance in this section and Sec. 10.4.3 provide options for defining the lower limit of quantitation.

10.4.2.1 To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. When using a multi-point calibration curve approach, every effort should be made to attain an acceptable correlation coefficient based on a linear response for each desired target analyte. If the recommended linear response cannot be attained using a minimum of three non-zero calibration standards, consideration should be given to adding more standards, particularly at the lower concentrations, in order to better define the linear range and the lower limit of quantitation. Conversely, the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. As with the single point calibration option, the multi-point calibration should be verified with both a mid- and low-level ICV standard analysis using the same 90 - 110% and 70 - 130% acceptance criteria, respectively.

10.4.2.2 Many instrument software packages allow multi-point calibration curves to be "forced" through zero. It is acceptable to use this feature, provided that the resulting calibration meets the acceptance criteria, and can be verified by acceptable QC results. Forcing a regression through zero should NOT be used as a rationale for reporting results below the calibration range defined by the lowest standard in the calibration curve.

10.4.3 After initial calibration, the calibration curve should be verified by use of an initial calibration verification (ICV) standard analysis. At a minimum, the ICV standard should be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for this mid-range ICV standard should be ±10% of its true value. Additionally, a low-level initial calibration verification (LLICV) standard should be prepared, using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation. The suggested acceptance criteria for the LLICV is ±30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification, with the exception that analyses may continue for those analytes that fail the criteria with an understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lowest standard. In some cases depending on the stated project data quality objectives, it may be appropriate to report these results as estimated, however, they should be qualified by noting the results are below the lower limit of quantitation. Therefore, the laboratory's

quantitation limit cannot be reported lower than either the LLICV standard used for the single point calibration option or the low calibration and/or verification standard used during initial multi-point calibration. If the calibration curve cannot be verified within these specified limits for the mid-range ICV and LLICV analyses, the cause needs to be determined and the instrument recalibrated before samples are analyzed. The analysis data for the initial calibration verification analyses should be kept on file with the sample analysis data.

10.4.4 Both the single and multi-point calibration curves should be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near the mid-range concentration. For the curve to be considered valid, the acceptance criteria for the CCV standard should be ±10% of its true value and the CCB should contain target analytes less than the established lower limit of quantitation for any desired target analyte. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB should be kept on file with the sample analysis data.

The low level continuing calibration verification (LLCCV) standard should also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis, i.e., every 10 samples may be necessary if low-level sample concentrations are anticipated and the system stability at low end of the calibration is questionable. In addition, the analysis of a LLCCV on a more frequent basis will minimize the number of samples for re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard should be made from the same source as the initial calibration standards at the established lower limit of quantitation as reported by the laboratory. The acceptance criteria for the LLCCV standard should be ± 30% of its true value. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. The instrument may need to be recalibrated or the lower limit of quantitation adjusted to a concentration that will ensure a compliant LLCCV analysis. The analysis data for the LLCCV standard should be kept on file with the sample analysis data.

10.5 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hr, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Sec. 4.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed.

NOTE: Analysts have noted improved performance in calibration stability if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 or 10 min before the calibration blank is run.

10.6 The linear dynamic range is established when the system is first setup, or whenever significant instrument components have been replaced or repaired, and on an as needed basis only after the system has been successfully calibrated using either the single or multi-point standard calibration approach.

The upper limit of the linear dynamic range needs to be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. A standard at the upper limit should be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply a spectral correction, the correction may not be valid and those analytes where the spectral correction has been applied may be inaccurately reported.

NOTE: Some metals may exhibit non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows it; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.998 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and/or recalculated on a daily basis using the same calibration verification QC checks as a linear calibration curve. Since these curves are much more sensitive to changes in operating conditions than the linear lines, they should be checked whenever there have been moderate equipment changes. Under these calibration conditions, quantitation is not acceptable above or below the calibration standards. Additionally, a non-linear curve should be further verified by calculating the actual recovery of each calibration standard used in the curve. The acceptance criteria for the calibration standard recovery should be ±10% of its true value for all standards except the lowest concentration. A recovery of ±30% of its true value should be achieved for the lowest concentration standard.

10.7 The analyst should (1) verify that the instrument configuration and operating conditions satisfy the project-specific analytical requirements and (2) maintain quality control data that demonstrate and confirm the instrument performance for the reported analytical results.

11.0 PROCEDURE

11.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater and other aqueous samples designated for a dissolved metals determination which have been prefiltered and acidified will not need acid digestion. However, all associated QC samples (i.e., method blank, LCS and MS/MSD) must undergo the same filtration and acidification procedures. Samples which are not digested must be matrix-matched with the standards. Solubilization and digestion procedures are presented in Chapter Three, "Inorganic Analytes."

CAUTION: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L (use 2.0 mL of 7.4.12 per 100 mL of sample) to preserve the mercury and to prevent it from plating out in the sample introduction system.

11.2 Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.

11.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

11.4 Operating conditions -- The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 min for the instrument to equilibrate before analyzing any samples. This must be verified by an analysis of the tuning solution (Sec. 7.10) at least four integrations with relative standard deviations of • 5% for the analytes contained in the tuning solution.

CAUTION: The instrument should have features that protect itself from high ion currents. If not, precautions must be taken to protect the detector from high ion currents. A channel electron multiplier or active film multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

11.5 Calibrate the instrument following the procedure outlined in Sec. 10.0.

11.6 Flush the system with the rinse blank solution (Sec. 7.6.3) until the signal levels return to the DQO or method's levels of quantitation (usually about 30 sec) before the analysis of each sample (see Sec. 10.0). Nebulize each sample until a steady-state signal is achieved (usually about 30 sec) prior to collecting data. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

11.7 Regardless of whether the initial calibration is performed using a single high standard and the calibration blank or the multi-point option, the laboratory should analyze an LLCCV (Sec. 10.4.4). For all analytes and determinations, the laboratory must analyze an ICV and LLICV (Sec. 10.4.3) immediately following daily calibration. It is recommended that a CCV LLCCV, and CCB (Sec. 10.4.4) be analyzed after every ten samples and at the end of the analysis batch.

11.8 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 10.2 and 10.4). Alternatively apply solid phase chelation chromatography to eliminate the matrix as described in Sec. 4.4.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values must be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All results should be reported with up to three significant figures.

12.2 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations must include appropriate interference corrections (see Sec. 4.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

12.3 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 In an EPA multi-laboratory study (Ref. 12), twelve laboratories applied the ICP-MS technique to both aqueous and solid samples. Table 3 summarizes the method performance data for aqueous samples. Performance data for solid samples are provided in Table 4. These data are provided for guidance purposes only.

13.3 Table 5 summarizes the method performance data for aqueous and sea water samples with interfering elements removed and samples preconcentrated prior to analysis. Table 6 summarizes the performance data for a simulated drinking water standard. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Hg	0.0	0.020
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.050
V	0.0	0.200
Zn	0.0	0.100

These data are provided for guidance purposes only.

TABLE 2
RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	Mass(es)
Aluminum	**27**
Antimony	121, **123**
Arsenic	**75**
Barium	138, 137, 136, **135**, 134
Beryllium	**9**
Bismuth (IS)	209
Cadmium	**114**, 112, **111**, 110, 113, 116, 106
Calcium (I)	42, 43, **44**, 46, 48
Chlorine (I)	35, 37, (77, 82)[a]
Chromium	**52**, **53**, **50**, 54
Cobalt	**59**
Copper	**63**, **65**
Germanium (IS)	74
Holmium (IS)	165
Indium (IS)	**115**, 113
Iron (I)	**56**, **54**, **57**, 58
Lanthanum (I)	139
Lead	**208**, **207**, **206**, 204
Lithium (IS)	6[b], 7
Magnesium (I)	24, **25**, **26**
Manganese	**55**
Mercury	202, **200**, 199, 201
Molybdenum (I)	98, 96, 92, **97**, 94, (108)[a]
Nickel	58, **60**, 62, **61**, 64
Potassium (I)	**39**
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, **78**, **82**, **76**, **77**, 74
Silver	**107**, **109**
Sodium (I)	**23**
Terbium (IS)	159
Thallium	**205**, 203
Vanadium	**51**, **50**
Tin (I)	120, **118**
Yttrium (IS)	89
Zinc	64, **66**, **68**, **67**, 70

[a] These masses are also useful for interference correction (Sec. 4.2).
[b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

NOTE: Method 6020 is recommended for only those analytes listed in Sec.1.2. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

TABLE 3

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	16 - 16	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique (ICP-AES or GFAA).

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). A larger number gives a more reliable comparison.

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 4

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	19 - 34	15 - 16	7
Beryllium	50 - 87	8.6 - 14	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique.

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value).

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 5

EXAMPLE METHOD PERFORMANCE DATA FOR AQUEOUS AND SEA WATER SAMPLES[A]
WITH INTERFERING ELEMENTS REMOVED
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]		
		9.0 mL	27.0 mL	CERTFIED
Manganese	55	1.8±0.05	1.9±0.2	1.99±0.15
Nickel	58	0.32±0.018	0.32±0.04	0.30±0.04
Cobalt	59	0.033±0.002	0.028±0.003	0.025±0.006
Copper	63	0.68±0.03	0.63±0.03	0.68±0.04
Zinc	64	1.6±0.05	1.8±0.15	1.97±0.12
Copper	65	0.67±0.03	0.6±0.05	0.68±0.04
Zinc	66	1.6±0.06	1.8±0.2	1.97±0.12
Cadmium	112	0.020±0.0015	0.019±0.0018	0.019±0.004
Cadmium	114	0.020±0.0009	0.019±0.002	0.019±0.004
Lead	206	0.013±0.0009	0.019±0.0011	0.019±0.006
Lead	207	0.014±0.0005	0.019±0.004	0.019±0.006
Lead	208	0.014±0.0006	0.019±0.002	0.019±0.006

Data obtained from Ref. 12.
[A] The dilution of the sea-water during the adjustment of pH produced 10 mL samples containing 9 mL of sea-water and 30 mL samples containing 27 mL of sea-water. Samples containing 9.0 mL of CASS-2, n=5; samples containing 27.0 mL of CASS-2, n=3.
[B] Concentration (ng/mL) ± 95% confidence limits.

These data are provided for guidance purposes only.

TABLE 6

ANALYSIS OF NIST SRM 1643b, TRACE METALS IN WATER[A]
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]	
		DETERMINED	CERTFIED
Manganese	55	30±1.3	28±2
Nickel	58	50±2	49±3
Cobalt	59	27±1.3	26±1
Nickel	60	51±2	49±3
Copper	63	23±1.0	21.9±0.4
Zinc	64	67±1.4	66±2
Copper	65	22±0.9	21.9±0.4
Zinc	66	67±1.8	66±2
Cadmium	111	20±0.5	20±1
Cadmium	112	19.9±0.3	20±1
Cadmium	114	19.8±0.4	20±1
Lead	206	23±0.5	23.7±0.7
Lead	207	23.9±0.4	23.7±0.7
Lead	208	24.2±0.4	23.7±0.7

Data obtained from Ref. 12.

[A] 5.0 mL samples, n=5.
[B] Concentration (ng/mL) ± 95% confidence limits.

These data are provided for guidance purposes only.

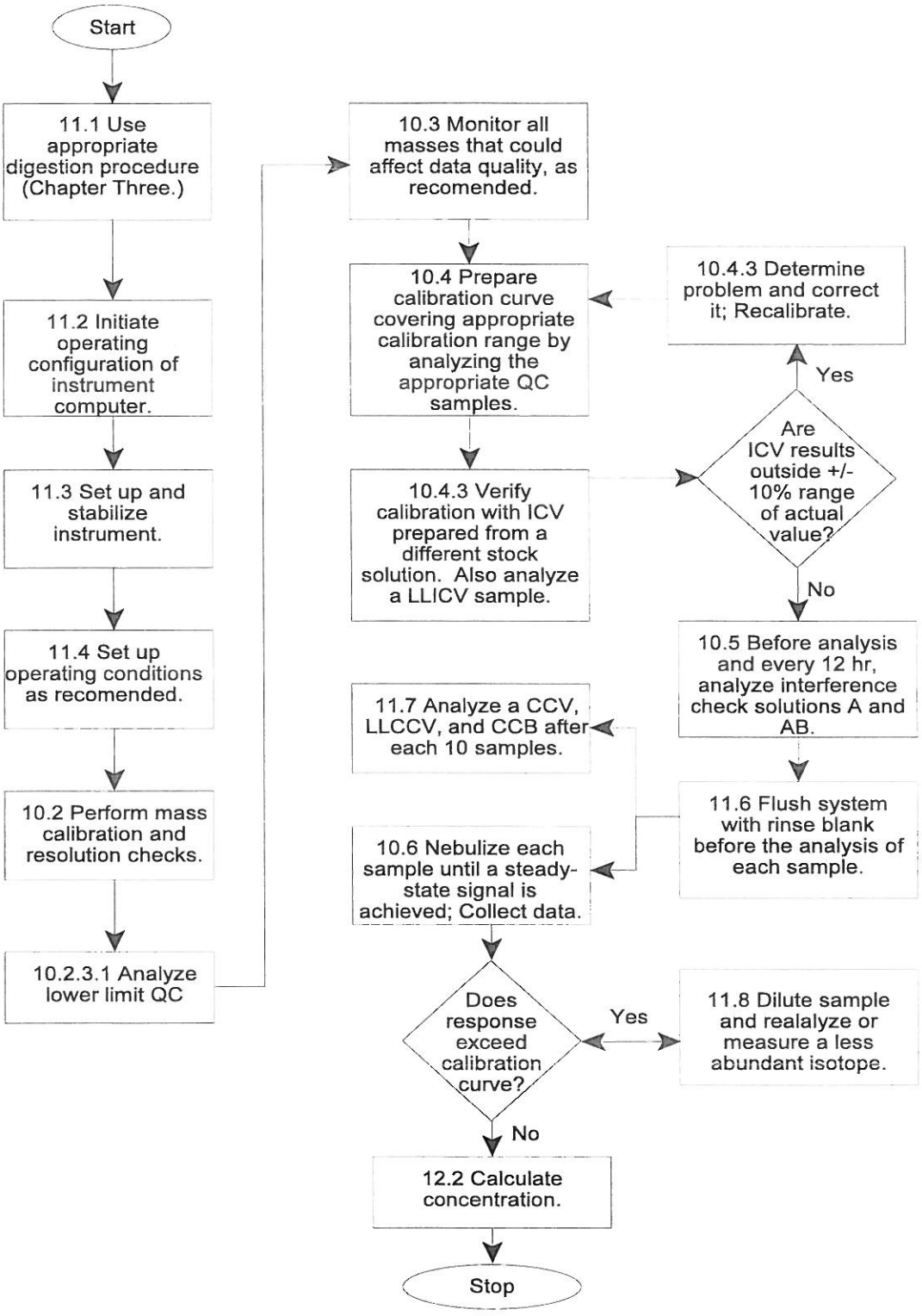
TABLE 7

COMPARISON OF TOTAL MERCURY RESULTS IN HEAVILY CONTAMINATED SOILS

Soil Sample	Mercury in µg/g	
	ICP-MS	CVAA
1	27.8	29.2
2	442	376
3	64.7	58.2
4	339	589
5	281	454
6	23.8	21.4
7	217	183
8	157	129
9	1670	1360
10	73.5	64.8
11	2090	1830
12	96.4	85.8
13	1080	1190
14	294	258
15	3300	2850
16	301	281
17	2130	2020
18	247	226
19	2630	2080

Source: Ref. 16.
These data are provided for guidance purposes only.

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



Designation: D6966 – 13

Standard Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Determination of Metals[1]

This standard is issued under the fixed designation D6966; 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 practice covers the collection of settled dust on surfaces using the wipe sampling method. These samples are collected in a manner that will permit subsequent extraction and determination of target metals in the wipes using laboratory analysis techniques such as atomic spectrometry.

1.2 This practice does not address the sampling design criteria (that is, sampling plan which includes the number and location of samples) that are used for clearance, hazard evaluation, risk assessment, and other purposes. To provide for valid conclusions, sufficient numbers of samples should be obtained as directed by a sampling plan, for example, in accordance with Guide D7659.

1.3 This practice contains notes that are explanatory and are not part of the mandatory requirements of this practice.

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

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:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D4840 Guide for Sample Chain-of-Custody Procedures

D7659 Guide for Strategies for Surface Sampling of Metals and Metalloids for Worker Protection

D7707 Specification for Wipe Sampling Materials for Beryllium in Surface Dust

E1792 Specification for Wipe Sampling Materials for Lead in Surface Dust

3. Terminology

3.1 For definitions of terms not listed here, see Terminology D1356.

3.2 *Definitions:*

3.2.1 *batch, n*—a group of field or quality control (QC) samples that are collected or processed together at the same time using the same reagents and equipment.

3.2.2 *sampling location, n*—a specific area within a sampling site that is subjected to sample collection.

3.2.2.1 *Discussion*—Multiple sampling locations are commonly designated for a single sampling site (see 3.2.3).

3.2.3 *sampling site, n*—a local geographic area that contains the sampling locations (see 3.2.2).

3.2.3.1 *Discussion*—A sampling site is generally limited to an area that is easily covered by walking.

3.2.4 *wipe, n*—a disposable towellette that is moistened with a wetting agent. (E1792)

3.2.4.1 *Discussion*—These towellettes are used to collect samples of settled dust on surfaces for subsequent determination of metals content in the collected dust.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *field blank, n*—a wipe (see 3.2.4) that is exposed to the same handling as field samples except that no sample is collected (no surface is actually wiped).

3.3.1.1 *Discussion*—Analysis results from field blanks provide information on the analyte background level in the wipe, combined with the potential contamination experienced by samples collected within the batch (see 3.2.1) resulting from handling.

4. Summary of Practice

4.1 Wipe samples of settled dust are collected on surfaces from areas of known dimensions with wipes satisfying certain requirements, using a specified pattern of wiping.

4.2 The collected wipes are then ready for subsequent sample preparation and analysis for the measurement of metals of interest.

[1] This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

Current edition approved April 1, 2013. Published April 2013. Originally approved in 2003. Last previous edition approved in 2008 as D6966 - 08. DOI: 10.1520/D6966-13.

[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.

5. Significance and Use

5.1 This practice is intended for the collection of settled dust samples for the subsequent measurement of target metals. The practice is meant for use in the collection of settled dust samples that are of interest in clearance, hazard evaluation, risk assessment, and other purposes.

5.2 This practice is recommended for the collection of settled dust samples from hard, relatively smooth nonporous surfaces. This practice is less effective for collecting settled dust samples from surfaces with substantial texture such as rough concrete, brickwork, textured ceilings, and soft fibrous surfaces such as upholstery and carpeting. Collection efficiency for metals such as lead from smooth, hard surfaces has been found to exceed 75 % (E1792).

6. Apparatus and Materials

6.1 *Sampling Templates*—One or more of the following: 10 cm by 10 cm (minimum dimensions) reusable or disposable aluminum or plastic template(s), or disposable cardboard templates, (full-square, rectangular, square "U-shaped," rectangular "U-shaped," or "L-shaped," or both); or templates of alternative areas having accurately known dimensions (see Note 1). Templates shall be capable of lying flat on a surface.

NOTE 1—For most surfaces, it is recommended to collect settled dust from a minimum surface area of 100 cm^2 to provide sufficient material for subsequent laboratory analysis. However, larger areas (for example, 30 cm by 30 cm) may be appropriate for surfaces having little or no visible settled dust, while a smaller sampling area (for example, 10 cm by 10 cm) may be appropriate for surfaces with high levels of visible settled dust. It is recommended to have a suite of templates with various sampling dimensions.

6.2 *Wipes,* for collection of settled dust samples from surfaces. Wipes shall be individually wrapped and fully wetted. The background metal(s) content of the wipes should be as low as possible. At a maximum, the background level of target metal(s) shall be no more than one-tenth the target concentration the metal(s) to be measured.

NOTE 2—Wipes meeting the requirements of Specifications E1792 or D7707, or both, may be suitable.

NOTE 3—Wipes made of cellulosic materials may produce fewer analysis problems than wipes made of synthetic polymeric materials.

6.3 *Sample Containers,* sealable, rigid-walled, 30-mL minimum volume.

NOTE 4—Screw-top plastic centrifuge tubes are an example of a suitable rigid-walled sample container.

NOTE 5—Use of a sealable plastic bag for holding and transporting the settled dust wipe sample is not recommended due to the potential loss of collected dust within the plastic bag during transportation and laboratory handling. Quantitative removal and processing of the settled dust wipe sample by the laboratory is significantly improved through the use of sealable rigid-walled containers.

6.4 *Measuring Tool,* tape or ruler, capable of measuring to the nearest ±0.1 cm.

6.5 *Plastic Gloves,* powderless.

6.6 *Cleaning Cloths,* for cleaning of templates and other equipment.

NOTE 6—Wipes used for dust sampling (6.2) can be used for cleaning templates and other sampling equipment, but other cleaning cloths or wipes not meeting the requirements described in (6.2) may be suitable for this purpose.

6.7 *Adhesive Tape,* suitable for securing the template(s) to the surface(s) to be sampled, and for demarcating sampling areas if templates are not used.

NOTE 7—Masking tape, for example, functions well for these purposes.

6.8 *Disposable Shoe Covers,* optional.

7. Procedure

7.1 Use one of the following two options when collecting settled dust samples from each sampling location. For wide, flat locations, it is recommended to use the template-assisted sampling procedure (see 7.1.1.2(a)). For small locations (for example, window sill, section of a piece of equipment, or portion of a vehicle interior), it will ordinarily be necessary to use the confined-area sampling procedure (see 7.1.1.2(b)).

NOTE 8—Metal contamination problems during field sampling can be severe and may affect subsequent wipe sample analysis results. Contamination can be minimized through frequent changing of gloves, use of shoe covers (see 6.8), and regular cleaning of sampling equipment with cleaning cloths (see 6.6). Use of disposable shoe covers between different locations, and removal of them prior to leaving the sampling site or entering vehicles, can be helpful in minimizing inadvertent transfer of contaminated dust from one location to another.

7.1.1 *Sampling Procedure:*

7.1.1.1 Don a pair of clean, powderless, plastic gloves (see 6.5 and Note 8).

7.1.1.2 Use either a template-assisted sampling procedure (a) or tape-defined sampling procedure (b):

(a.) Carefully place a clean template on the surface to be sampled in a manner that minimizes disturbance of settled dust at the sampling location. Tape the outside edge of the template to prevent the template from moving during sample collection.

(b.) Alternatively, mark the defined area to be sampled with adhesive tape (6.7) being careful not to disturb the settled dust, and measure the area to be sampled using the measuring tool (6.4).

7.1.1.3 Obtain a wipe (6.2) and, if there is a possibility for the package containing the wipe to be contaminated with dust, clean the outside of the package with a cleaning cloth (6.6).

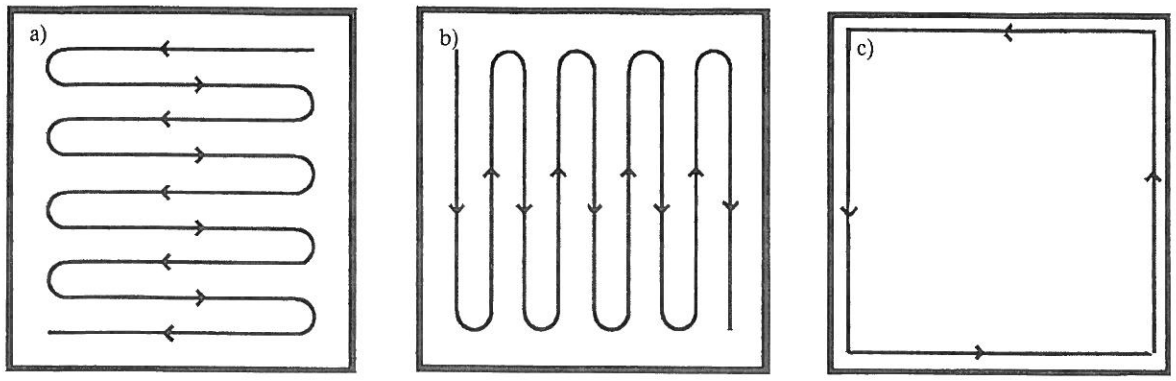
7.1.1.4 Remove the wipe from its package, and inspect the wipe to ensure that it is fully wetted and not contaminated with dust or other material. Discard the wipe if it is found to be too dry or contaminated, or both.

7.1.1.5 Using an open flat hand with the fingers together, place the wipe on the surface to be sampled. Wipe the selected surface area, side to side, in an overlapping "S" or "Z" pattern while applying pressure to the fingertips (refer to Figs. 1 and 2). Wipe the surface so that the entire selected surface area is covered. Perform the wiping procedure using the fingers and not the palm of the hand.

7.1.1.6 Repeat 7.1.1.5 using a different brand of wipe (after selecting a different sampling location) if the wipe originally used significantly changes shape (for example, rolls up by curling) or tears during the wiping process.

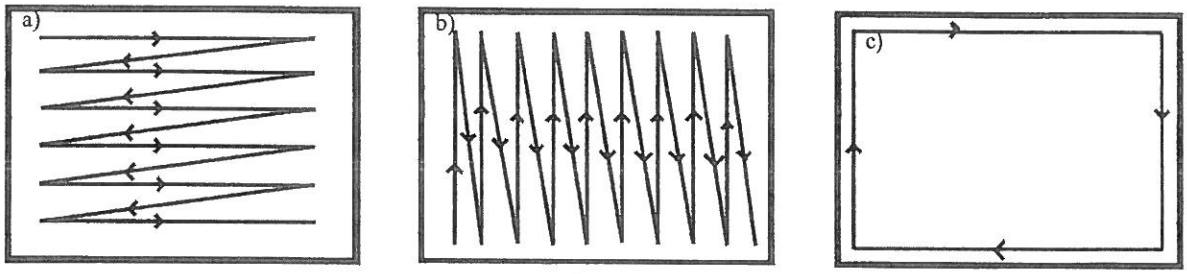
NOTE 9—Some surfaces (for example, rough surfaces) may cause certain wipes to curl up or otherwise significantly change shape during the wiping process. A type of wipe that maintains its integrity should be selected for each surface sampled.

7.1.1.7 Fold the wipe in half with the collected dust side folded inward and repeat the preceding wiping procedure



NOTE 1—Only the center of the wiping path is shown, not the entire wiping width. Fig. 1a) shows the first "S" wiping pattern over the surface area to be sampled; Fig 1b) demonstrates the second "S" wiping course over the surface; and Fig. 1c) shows the final wiping which is targeted toward edges and corners.

FIG. 1 Schematic of a Side-to-Side Overlapping "S" Wiping Pattern



NOTE 1—Only the center of the wiping path is shown, not the entire wiping width. Fig. 2a) shows the first "Z" wiping pattern over the surface area to be sampled; Fig 2b) demonstrates the second "Z" wiping course over the surface; and Fig. 2c) shows the final wiping which is targeted toward edges and corners.

FIG. 2 Schematic of a Side-to-Side Overlapping "Z" Wiping Pattern

(7.1.1.5) within the selected sampling area using an up and down overlapping "S" or "Z" pattern at right angles to the first wiping (see Figs. 1 and 2 and Note 10).

NOTE 10—Wipes are folded to envelop the collected dust within the wipe, to avoid loss of the collected dust, and to expose a clean wipe surface for further dust collection from the sampling location. For sample areas containing large amounts of settled dust, carefully wipe the area to ensure as much dust as possible within the wipe is captured.

7.1.1.8 Fold the wipe in half again with the collected dust side folded inward and repeat the wiping procedure one more time, concentrating on collecting settled dust from edges and corners within the selected surface area (see Figs. 1 and 2 and Note 10).

7.1.1.9 Fold the wipe again with the collected dust side folded inward and insert the wipe into a sample container (6.3).

7.1.1.10 Label the sample container with sufficient information to uniquely and indelibly identify the sample.

7.1.1.11 Record the dimensions (in square centimetres) of the selected sampling area (that is, the internal dimensions defined by the template or the taped area) or that the sample is a blank.

7.1.1.12 Discard the gloves.

7.2 Collect field blanks at a minimum frequency of 5 % (at least one field blank for every 20 wipe samples collected). The minimum number of field blanks to collect for each batch of wipe samples used should be three. Place field blanks in sample containers and label these samples in the same fashion as the collected surface dust samples (see 7.1.1.10).

7.3 Follow sampling chain of custody procedures to ensure sample traceability. Ensure that the documentation which accompanies the samples is suitable for a chain of custody to be established in accordance with Guide D4840.

8. Records

8.1 Field data related to sample collection shall be documented in a sample log form or field notebook (see Note 11). If field notebooks are used, then they shall be bound with pre-numbered pages. All entries on sample data forms and field notebooks shall be made using ink, with the signature and date of entry. Any entry errors shall be corrected by using only a single line through the incorrect entry (no scratch outs), accompanied by the initials of the person making the correction, and the date of the correction (see Note 12).

NOTE 11—Field notebooks are useful for recording field data even when preprinted sample data forms are used.

NOTE 12—These procedures are important to properly document and trace field data.

8.2 At a minimum, the following information shall be documented:

8.2.1 Project or client name, address, and city/state/country location.

8.2.2 General sampling site description.

8.2.3 Information as to the specific collection protocol used (for example, template-assisted; "Z"-wiping pattern, etc.).

8.2.4 Information as to the specific type or brand of wipes used, including manufacturer and lot number.

8.2.5 Information on quality control (QC) samples: which samples are associated with what group of field blanks.

8.2.6 For each sample collected (including field blanks): an individual and unique sample identifier and date of collection. This information shall be recorded on the sample container in addition to the field documentation.

8.2.7 For field samples (not including field blanks), record in field documentation (field notebook or sample log form) the dimensions of each area sampled (in square centimetres).

8.2.8 For each sample collected: name of person collecting the sample, and specific sampling location information from which the sample was removed.

9. Keywords

9.1 metals measurement; sample collection; settled dust; surfaces; wipe

Designation: D6661 – 10

Standard Practice for Field Collection of Organic Compounds from Surfaces Using Wipe Sampling[1]

This standard is issued under the fixed designation D6661; 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 practice addresses sampling of organic compounds (i.e., PCBs, dioxins, many pesticides and similar compounds) from smooth nonporous surfaces using a solvent-wetted wipe sampling method. Samples are collected in a manner that permits the solvent extraction of the organic compound(s) of interest from the wipes and subsequent determination using a laboratory analysis technique such as gas chromatography with a suitable detector. This practice is, however, unsuitable for the collection of volatile organic compounds.

1.2 This practice should only be used to collect samples for the determination of organic compound(s) on a loading basis (e.g., mass per unit area). It cannot be used to collect samples for the determination of organic compounds on a concentration basis (e.g., mass per unit mass).

1.3 This wipe sampling practice is not recommended for collecting samples of organic compounds from rough or porous surfaces such as upholstery, carpeting, brick, rough concrete, ceiling tiles, and bare wood. It is also not intended for the collection of dust samples (see Practice E1278) or sampling to estimating human exposure to contaminated surfaces.

1.4 To ensure valid conclusions are reached, a sufficient number of samples must be obtained as directed by a sampling design (the number and location of samples including quality control samples) and a quality assurance/quality control plan. This practice does not address the sampling designs used to achieve the data quality objectives (see Practice D5792).

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:*[2]

D4687 Guide for General Planning of Waste Sampling

D5681 Terminology for Waste and Waste Management

D5792 Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives

E1278 Guide for Radioactive Pathway Methodology for Release of Sites Following Decommissioning (Withdrawn 2005)[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D5681.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *wipe, n*—sorbent material (e.g., cotton gauze) that is rubbed on a surface to collect a sample for chemical analysis.

4. Summary of Practice

4.1 A wipe sample is collected from a smooth nonporous surface with a solvent-wetted wipe following a specified pattern of wiping to ensure complete coverage of an area of specified dimensions. The wipe is then extracted and analyzed to detect and quantify (at least semiquantitatively) the presence of organic compounds on surfaces.

5. Significance and Use

5.1 Wipe sampling is typically used by persons involved in hazardous waste site investigations to characterize the areal extent and the level of contamination on walls, floors, equipment, etc. Wipe sampling is also used to determine compliance with regulations.

5.2 There are many factors that contribute to variation in sampling results during wipe sampling including, the use of different pressures applied to the wipe, different kinds of wipes,

[1] This practice is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.02 on Sampling Techniques.

Current edition approved Dec. 1, 2010. Published January 2011. Originally approved in 2001. Last previous edition approved in 2006 as D6661-01 (2006). DOI: 10.1520/D6661-10.

[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.

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

TABLE 1 Contaminant Recovery Data Using Common Solvents and TLC Pads[4]

Compound	Solvent	Percent Recovery
Chlordane	Acetone	71
	Isooctane	54
Chlorpyrifos	Acetone	72
	Isooctane	56
Malathion	Dichloromethane	81
	Isooctane	80
Diazinon	Isooctane	70
Aroclor 1260	Isooctane	80
	Acetone	76
Bendiocarb	Acetone	85
	Isopropanol	84
Propoxur	Isopropanol	96
	Acetone	90

different wiping patterns, the texture of the surface being wiped, and perhaps even the duration of wiping. The significance of this practice is that it standardizes wiping procedures to reduce sampling variability in the collection of samples from smooth, nonporous surfaces such as metal, glass, painted or sealed surfaces, tile, etc., in and around buildings, and from pipes, tanks, decontaminated equipment, etc.

6. Sampling Equipment and Supplies

6.1 *Sample Containers*—Airtight amber glass sample containers with PTFE-lined caps such as 40-mL volatile organic analysis vials are recommended. Larger 125-mL wide mouth bottles may also be used which eliminate the need for forceps to place or remove wipes from the sample container. To minimize solvent handling in the field, wipes may be wetted with solvent in the laboratory and shipped to the field in the sample container.

6.2 *Wipes*—Cotton gauze pads 7.6-cm square are to be used. Sterile surgical gauze pads are typically used without precleaning however, samples of the pads should be analyzed or otherwise determined to be free of the target compounds and substances that could interfere with the analytical method. If necessary, pads should be precleaned by solvent extraction in a laboratory prior to field use.

6.3 *Solvent*—A high purity solvent (one which is free of contaminants that might interfere with analysis), capable of solublizing the target organic compound and compatible with the surface being wiped, should be used. For collecting PCBs and most pesticides (e.g., chlordane, chlorpyrifos and malathion) isooctane is an effective solvent. For carbamates or known polar pesticides, isopropanol is more effective. Some guidance on solvent selection (Table 1) was generated by EPA[4] using thin layer chromatography (TLC) saturation pads (essentially a heavy filter paper) which generally performs similarly to cotton gauze pads. Hexane is another commonly used solvent to consider for PCB sampling. Some effective solvents such as acetone are not the most desirable because interfering compounds from some surfaces can also be recovered.[4] The analytical laboratory should be able to assist in selecting a proper wiping solvent compatible with the surface to be sampled and with the analytical procedures.

6.4 *Disposable Gloves*—Powderless gloves which protect the sampler's hands from the solvent and do not contribute any possibly interfering contaminants should be used. A new pair of gloves should be used for each wipe.

6.5 *Sampling Template (Optional)*—Templates made of stainless steel, aluminum, disposable heavy-duty aluminum foil or other inert material can be used to expose a 10-cm by 10-cm surface area to be wiped.

6.6 *Other*—Standard field sampling supplies are discussed in Guide D4687 and may include a copy of the sampling plan, chain-of-custody forms, custody seals, logbook, camera, field data sheets, sample labels, forceps, noncontaminating marker (e.g., pencil, scribe), decontamination supplies, and solvent dispenser. Additional detailed equipment lists are included in EPA publications.[5, 6]

7. Procedure

7.1 Review the sampling plan and sampling procedures, assemble sampling equipment, ensure personnel are adequately trained for their tasks, arrange logistics, and ensure supplies will be available at the site when needed. Since sampling results can vary between operators sampling identical surfaces, the same person should collect all wipe samples at a given site[5] to minimize variability and enhance comparison of results from various locations.

7.2 Locate the sampling points as specified in, or according to the guidance of, the sampling plan.

7.3 Install the sample template or otherwise delineate the area to be sampled, normally a 10-cm by 10-cm area. This can be achieved by either taping a template in place (caution, tape used to secure a template should not be wiped since this may contaminate the sample), or by drawing the boundary of the area to be sampled with a noncontaminating marker. Although a 10-cm by 10-cm area is the standard-size template, the area does not have to be square as long as a 100-cm^2 area is being sampled. If contaminant levels are expected to be low, greater sensitivity may be achieved by sampling a larger area. In all cases, the location and dimensions (e.g., length, width, diameter) of the area sampled must be recorded and possibly photographed.

7.4 Don a new glove and obtain a clean wipe. If precleaned wipes were shipped in sample containers, forceps can be used to remove the wipe from the container.

7.5 If solvent-wetted wipes were not shipped to the field, dispense solvent (2 mL recommended although somewhat more may be desired if shipping solvent-wetted wipes to the field in 125-mL bottles) onto the cotton gauze pad. A repeating dispenser can be used for dispensing the same amount of

[4] Carr, B. L. and Hill, D. F., *Sampling of Common Pesticides and PCBs from Inert Surfaces, EPA 330/1-90-001, National Enforcement Investigations Center, Denver, CO, 1989.*

[5] Smith, J. H., *Wipe Sampling and Double Wash/Rinse Cleanup as Recommended by the Environmental Protection Agency PCB Spill Cleanup Policy, U.S. Environmental Protection Agency, Washington, DC, 1991* .

[6] U.S. Environmental Protection Agency, *Chip, Wipe and Sweep Sampling, SOP#: 2011, Environmental Response Team, NJ, 1994.*

solvent to each wipe. The EPA's PCB program specifies the use of a saturated, but not dripping, wipe (~5 mL of solvent),[5] which may slightly increase contaminant recovery, but research has shown more consistent results using 2 mL of solvent.[4]

7.6 Wipe the entire surface to be sampled using firm strokes by pressing with the fingertips. Wipe vertically and then horizontally to ensure there is complete coverage in both directions with minimal overlap of the previous stroke. The objective is to systematically, thoroughly, and consistently wipe the entire target area twice, each time from a different direction.[5] Excess wiping (e.g., more than single coverage in each direction) has been shown to reduce organic contaminant recovery.[4]

7.7 Fold the wipe with the sampled side inward, place it in the sample container, and cap the container. EPA's PCB program specifies air drying the saturated cotton gauze pad, either in the laboratory or the field. Field drying can be accomplished by placing wipes on clean aluminum foil or in the sample container with the lid off (ensure no liquid solvent is lost when placing wet wipes in the sample jar).

7.8 Label the sample container and complete standard documentation procedures.

7.9 Store the sample out of direct sunlight, cool to 4°C and ship or transport the sample(s) to the laboratory.

7.10 Quality control samples should be collected as specified in the sampling or quality assurance/quality control plan. The types of quality control samples may include blank, second wipe, duplicate, and spiked samples[5] as described below but may include other types as needed to achieve the objectives.

7.10.1 The first type of blank sample is a wipe in an unopened sample container (if provided to the field in this manner) or a clean wipe (with or without solvent) placed in a sample container. This type of blank is useful in determining whether the wipes and possibly the solvent are contaminated. The second type of blank is a wipe sample collected from a control area for each type of surface sampled. This type of blank is useful in determining whether contaminants may have been extracted from the surface sampled (e.g., target or interfering contaminants from painted, plastic, tile, etc. surfaces).

7.10.2 Two other types of quality control samples are second wipes and duplicate samples. A second wipe sample is collected from exactly the same area and immediately after the regular sample is collected. These sample results are used to estimate the residual contamination remaining after regular sampling. The data can be used to calculate an estimate of total surface contamination (this calculation is beyond the scope of this standard). This type of wipe is important for sampling relatively more porous surfaces such as vinyl tile. A duplicate sample is collected immediately adjacent to the regular sample and can be used to estimate sample collection precision (assuming the immediately adjacent area has the same level of contamination).

8. Keywords

8.1 sample collection; surface sample; wipe; wipe sample

METHOD 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed below for soil and sediment samples. Some common elements are not listed in this method because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). These light elements are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed below are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF. The following RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-0
Barium (Ba)	7440-39-3
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Thallium (Tl)	7440-28-0
Tin (Sn)	7440-31-5

Analytes	CAS Registry No.
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

In addition, the following non-RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Calcium (Ca)	7440-70-2
Iron (Fe)	7439-89-6
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-93-7
Potassium (K)	7440-09-7
Rubidium (Rb)	7440-17-7
Strontium (Sr)	7440-24-6
Thorium (Th)	7440-29-1
Titanium (Ti)	7440-32-6
Zirconium (Zr)	7440-67-7

1.2 This method is a screening method to be used with confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)). This method's main strength is that it is a rapid field screening procedure. The method's lower limits of detection are typically above the toxicity characteristic regulatory level for most RCRA analytes. However, when the obtainable values for precision, accuracy, and laboratory-established sensitivity of this method meet project-specific data quality objectives (DQOs), FPXRF is a fast, powerful, cost effective technology for site characterization.

1.3 The method sensitivity or lower limit of detection depends on several factors, including the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. Example lower limits of detection for analytes of interest in environmental applications are shown in Table 1. These limits apply to a clean spiked matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (100 -600 second) count times. These sensitivity values are given for guidance only and may not always be achievable, since they will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of performance-based sensitivity is presented in Sec. 9.6.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use either sealed radioisotope sources or x-ray tubes to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This latter process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples. The three electron shells include the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α), beta (β), or gamma (γ) etc., which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a K_α line is produced by a vacancy in the K shell filled by an L shell electron, whereas a K_β line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is on average 6 to 7 times more probable than the K_β transition; therefore, the K_α line is approximately 7 times more intense than the K_β line for a given element, making the K_α line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines (L_α and L_β) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than

the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.77 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments, specifically, in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

3.0 DEFINITIONS

3.1 FPXRF -- Field portable x-ray fluorescence.

3.2 MCA -- Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS -- Site-specific calibration standards.

3.4 FP -- Fundamental parameter.

3.5 ROI -- Region of interest.