Method 1001: Lead in Drinking Water by Differential Pulse Anodic Stripping Voltammetry

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Disclaimer

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Introduction

Method 1001 was developed by Palintest Ltd and Enviromed plc to provide a simple, rapid, low-cost procedure for the determination of lead in drinking water

Method 1001 is a performance-based method applicable to the determination of dissolved lead and total recoverable lead in drinking water Acid preserved or acid digested water samples are buffered, and analyzed by differential pulse anodic stripping voltammetry (DPASV) using pre-calibrated disposable sensors

Copies of the method can be obtained from, or questions concerning this method or its application should be addressed to:

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Method 1001

Lead in Drinking Water by Differential Pulse Anodic Stripping Voltammetry

1.0 Scope and Application

1.1 This method is for the determination of dissolved lead and total recoverable lead in drinking water.

1.2 Although this method has been approved for use in the Environmental Protection Agency's data gathering and monitoring programs under the Safe Drinking Water Act, it is prudent to check with the appropriate authority e.g., the Code of Federal Regulations, to verify current approval status.

1.3 This method is for the determination of lead, Chemical Abstracts Service Registry Number 7439-92-1.

1.4 This method is applicable to drinking water.

1.5 The method detection limit (MDL) was found to be 2 µg/L lead. This was calculated from analysis of seven aliquots of deionized water fortified with lead stock standard solution to 5 µg/L lead. The minimum level (ML) has been set at 5 µg/L.

1.6 The application range is 2 - 100 µg/L lead Higher concentrations may be determined by sample dilution provided that the analyst demonstrates that the performance of the method can be maintained with the accepted criteria.

1.7 This method is performance-based. The laboratory is permitted to omit any step or modify any procedure (e g , to overcome interferences, to lower the cost of measurements), provided that all performance requirements set forth in this method are met. The laboratory is not allowed to omit any quality control analyses. The terms "must", "may", and "should" are used in this method to illustrate the importance of the procedures essential in successfully analyzing samples and avoiding contamination; however, these procedures can be modified or omitted if the laboratory can show that data quality is not affected The requirements for establishing method equivalency are given in Section 9.1.2.

1.8 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5

1.9 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9 2.

2.0 Summary of Method

2.1 A 125-mL sample is taken and prepared by one of the following procedures

2.1.1 For dissolved lead, the sample is filtered to 0 45 µm and acidified to pH <2 to preserve for transportation

2.1.2 For total recoverable lead, the sample is acidified to pH <2 to preserve for transportation Samples must be acid digested before analysis.

2.2 A 50-mL aliquot of acid preserved or acid digested sample is neutralized with sodium hydroxide

2.3 A 5-mL portion of the neutralized sample is decanted to a sample tube, buffered to pH 4 and conditioned with an excess of supporting electrolyte to ensure precision of the analysis. A decomplexing agent is added to release lead from polyphosphate complexes.

2.4 The lead in the conditioned sample is determined by DPASV using a pre-calibrated disposable sensor. The lead in the sample is concentrated by plating onto the working electrode of the disposable sensor and then it is stripped back into solution by raising the electrode potential As the lead returns to solution a peak of current is detected The peak potential identifies the metal and the peak height is proportional to the concentration of the lead

2.5 The peak height is automatically converted to micrograms per liter of lead by reference to calibration curves stored in the instrument software The appropriate calibration is selected by keying the eight-digit calibration code for the batch of sensors

2.6 Quality is assured through calibration and verification with externally referenced standard solutions.

3.0 Definitions

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible

3.1 Units of weight and measure and their abbreviations :

3.1.1 Symbols :

°C	degrees Celsius
<	less than
%	percent
±	plus or minus

3.1.2 Alphabetical characters

L	liter
mg	milligram
mg/L	milligram per liter
mL	milliliter
µg	microgram
µg/L	microgram per liter
µm	micrometer

3.2 Definitions, acronyms, and abbreviations

3.2.1 Analyte The lead tested for by this method

3.2.2 Analytical batch The set of samples acid digested or analyzed at the same time, to a maximum of 20 samples Each analytical batch of 20 or fewer samples must be accompanied by a laboratory reagent blank (Section 9 3.1), an ongoing precision and recovery sample (OPR, Section 9.3.2), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.5), resulting in a minimum of five analyses (one sample, one blank, one OPR, one MS and one MSD) and a maximum of 24 analyses (twenty samples, one blank, one OPR, one MS and one MSD) in the batch. If greater than 20 samples are to be digested or analyzed at one time, the samples must be separated into analytical batches of 20 or fewer samples

3.2.3 Calibration blank (CB): A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

3.2.4 Calibration standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solution The CAL solutions are used to calibrate the instrument response with respect to analyte concentration

3.2.5 DPASV The analytical technique of differential pulse anodic stripping voltammetry

3.2.6 IPR See initial precision and recovery

3.2.7 Initial precision and recovery (IPR) Four aliquots of the diluted PAR analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method or instrumentation is modified

3.2.8 Laboratory reagent blank (LRB): An aliquot of reagent water or other blank matrix that is treated as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

3.2.9 Linear calibration range (LCR) The concentration range over which the instrument response is linear.

3.2.10 Matrix spike (MS) and matrix spike duplicate (MSD): Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are prepared and/or analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations

3.2.11 Material safety data sheet (MSDS): Written information provided for the chemical reagents concerning a chemical's toxicity health hazards, physical properties, fire, and reactivity data including storage, spill and handling precautions

3.2.12 Method detection limit (MDL) The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.2.13 Minimum level (ML): The lowest level at which the entire analytical system gives a recognisable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard

3.2.14 May. This action, activity, or procedural step is neither required nor prohibited

3.2.15 May not This action, activity, or procedural step is prohibited.

3.2.16 Must This action, activity, or procedural step is required.

3.2.17 Ongoing precision and recovery standard (OPR): An aliquot of reagent water or other blank matrix to which known quantities of the method analyte are added in the laboratory. The OPR is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements

3.2.18 Precision and recovery standard (PAR): Secondary standard that is diluted and spiked to form the IPR and OPR

3.2.19 Quality control sample (QCS): A solution of method analytes of known concentrations The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal calibration process.

3.2.20 Should This action, activity, or procedure step is suggested but not required.

4.0 Interferences

4.1 No interferences have been encountered with the chemical species found naturally in drinking water or added as treatment chemicals The method is without interference for the determination of 2 to 100 µg/L lead in the presence of at least 500 µg/L aluminium, 1000 µg/L chromium, 1000 µg/L cadmium, 1000 µg/L iron, 200 µg/L manganese, 5000 µg/L zinc, 5 mg/L chlorine, 10 mg/L sodium hexametaphosphate, 10 mg/l sodium tripolyphosphate, 800 mg/L chloride, 1 5 mg/L fluoride, 50 mg/L nitrate, 10 mg/L phosphate, 250 mg/L sulphate, 500 mg/l. $CaCO_3$ alkalinity, 500 mg/L $CaCO_3$ hardness.

4.2 The method 1001 is not appropriate for use on water samples believed to contain detergent residues, unless these are decomposed by acid digestion prior to analysis

4.3 The use of a pH meter with glass electrode to monitor pH during neutralization of the sample should be avoided. This causes contamination of the sample and erroneously high results.

5.0 Safety

5.1 Lead is a toxic element, and should be treated as a potential health hazard. Exposure to the standard solutions should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst

5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe working environment and a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of material safety data sheets (MSDS) should be available to all personnel involved in these analyses Additional information on laboratory safety can be found in References 16 1 to 16.3.

6.0 Equipment and Supplies

Note: *Brand names, suppliers and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Sampling equipment :

6.1.1 Sample collection bottles-glass, polyethylene or PTFE bottles These must be prepared by the method described in Section 6 3.3 for labware.

6.1.2 Membrane filter assembly and 0.45 µm membrane filters

6.2 Equipment for glassware cleaning :

6.2.1 Laboratory sink with overhead fume hood

6.3 Equipment for sample and standard preparation :

6.3.1 Analytical balance (capable of weighing 0.1 mg).

6.3.2 Laboratory glassware and plasticware required includes sample containers, volumetric flasks, pipets, conical beakers (250-mL), and watch glasses (50-mm).

6.3.3 Cleaning .

6.3.3.1 Labware should be thoroughly washed with laboratory-grade detergent and tap water, rinsed with tap water then deionized (DI) water, rinsed with (1+1) nitric acid, then tap water and finally thoroughly rinsed with DI water

Note: *Prolonged soaking of glassware with (1 + 1) nitric acid or chromic acid should be avoided as this causes a lead-demand on glass surfaces.*

If it can be documented through an active analytical quality control program using spiked samples, reagent and sample blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

6.3.4 Laboratory hot plate (capable of maintaining a temperature of 85°C).

6.4 Equipment for analysis :

6.4.1 Differential pulse anodic stripping voltammeter dedicated to the analysis of lead in drinking water is required, e g.

Palintest Scanning Analyzer SA-1000, or
Hach Company HSA-1000, or
Pace Environs Inc PaceScan 1000, or equivalent

6.4.2 Graduated plastic tubes and plastic crushing rods, cleaned as described in Section 6.3.3.

7.0 Reagents and Standards

7.1 Acids for sample preparation. Because of the high sensitivity of the method ultra high-purity reagents should be used whenever possible

7.1.1 Nitric acid, concentrated (sp. gr 1 41)

7.1.2 Nitric acid (1+1) Add 500 mL concentrated nitric acid to 500 mL of DI water and dilute to one liter

7.1.3 Hydrochloric acid, concentrated (sp. gr. 1.19).

7.2 Methyl orange indicator solution 0.1% solution. Dissolve 1.0g methyl orange in 200 mL DI water and make-up to one liter with DI water

7.3 Sodium hydroxide solution 6M Gradually dissolve 240g sodium hydroxide in 800 mL DI water, stirring continuously. Allow to cool periodically. Make-up to one liter with DI water

7.4 Sodium hydroxide solution 1.5M. Gradually dissolve 60g sodium hydroxide in 800 mL DI water, stirring continuously and allow to cool Make-up to one liter with DI water. (A Neutralization Pack consisting of 1 5M sodium hydroxide solution and methyl orange indicator solution (7.2) is available from Palintest, Catalogue No PT 429, or Hach Company Catalogue No 50405-00).

7.5 Sample conditioning tablets (Soluprep SP-A, Palintest catalogue number PT 425, or PrepTab™ PT-Pb contained in sensor pack, Hach Company Catalogue No 50401-00 or equivalent). Tablets contain potassium phthalate buffer (pH 4.0) supporting electrolyte and decomplexing reagent (trade secret). The nominal tablet weight is 0.1g and shelf-life a minimum of five years. The tablets are presented individually vacuum-sealed in foil packaging for maximum stability.

7.6 Disposable sensors (Palintest SE-1, catalogue number PT 425, or HSE-Pb contained in sensor pack, Hach Company Catalogue No 50401-00 or equivalent). For the determination of lead and copper in drinking water. Disposable sensors are manufactured in batches and a carefully selected representative sample of sensors is withdrawn from across the batch to prepare the calibration curve for the batch, by reference to a lead standard solution (NIST SRM 3128) The calibration curve is converted to an eight digit code which is specific to the batch of sensors To calibrate the instrument for use, this calibration code is keyed in and this selects the appropriate calibration curve from the instrument memory. The calibration code contains check digits to ensure the instrument rejects erroneously keyed codes. Disposable sensors have a shelf life of 12 months, and are marked with an expiry date

7.7 Stock standard solution (SSS). Prepare a 1000 mg/L lead stock standard solution as follows. Accurately weigh 1.5986g lead (II) nitrate ($Pb(NO_3)_2$) and dissolve in approximately 200 mL DI water. Add 10 mL concentrated nitric acid, mix and dilute to one liter with DI water. Prepare fresh every six months.

1.0 mL SSS = 1.0 mg Pb

7.7.1 All standard solutions prepared from the stock standard solution should be acidified with 2 mL concentrated nitric acid prior to dilution to volume.

7.7.2 Intermediate standard solution (ISS). Daily dilute 10 mL of SSS to a liter with DI water.

1.0 mL ISS = 10 µg Pb

7.7.3 Working calibration standards are prepared from ISS.

7.7.4 Solutions based on the SSS are used for preparation of CAL and MDL.

7.8 Independent standard. Prepare a lead solution by dilution of commercially available, NIST traceable (i e traceable to a primary standard) lead nitrate solution This standard should be obtained from a different source than the calibration standards

7.8.1 This solution is used for the preparation of QCS and OPR solutions and to fortify the sample matrix in the preparation of the MS and MSD

7.9 Deionized water (DI) ASTM Type I water or equivalent (Reference 16.4).

8.0 Sample Collection, Preservation and Storage

8.1 Prior to sample collection, consideration should be given to the type of data required so that appropriate preservation and pre-treatment steps can be taken Filtration, acid preservation, etc., should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 Collect samples in pre-cleaned, acid-rinsed, glass, polyethylene, or PTFE bottles

8.3 For the determination of dissolved lead, filter the sample through a 0 45-µm membrane filter. Use a proportion of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2. Normally, 3 mL of (1+1) nitric acid per liter of sample is sufficient.

8.4 For the determination of total recoverable lead, acidify with (1+1) nitric acid (3 mL per liter of sample) to pH <2 The sample may not be filtered prior to analysis.

8.5 Samples that cannot be acid preserved at the time of collection, because of sampling limitations or transport restriction, but which must be returned to the laboratory, should be acidified with (1+1) nitric acid to pH <2 on receipt in the laboratory. Following acidification, the sample should be held for a minimum of 16 hours before withdrawing an aliquot for sample processing.

9.0 Quality Control

9.1 Each laboratory using this method is required to operate a formal quality assurance program (Reference 16.5). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analyses of standards and blanks as a test of continued performance, and analyses of matrix spike (MS) and matrix spike duplicate (MSD) samples to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted certain options to improve or simplify sample pre-treatment or lower then costs of measurements, provided that all performance specifications are met Alternate determinative techniques, such as visible spectrophotometry, and changes that degrade method performance, are not allowed If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analyte of interest Specificity is defined as producing results equivalent to the results produced by this method for analytical standards (Section 9.2.2) and, where applicable, environmental samples (Section 9.5) , and that meet all of the QC criteria stated in this method

9.1.2.1 Each time a modification is made to this method, the analyst is required to repeat the IPR test in Section 9.2 5, to demonstrate that the modification produces results equivalent to or better than results produced by this method If the detection limit of the method will be affected by the modification, the analyst must demonstrate that the MDL (40 CFR Part 136, Appendix B) is less than or equal to the MDL for the analyte in this method, or one-third the regulatory compliance level, whichever is higher If the change will affect calibration, the analyst must recalibrate the instrument according to Section 10

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum .

9.1.2.2.1 The names, titles, addresses and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2 The analyte measured, by name and CASRN

9.1.2.2.3 A narrative stating reason(s) for the modification(s).

9.1.2.2.4 Results from all QC tests comparing the modified method to this method, including :

a) Calibration (Section 10)
b) Calibration verification (Section 9.4)
c) Initial precision and recovery (Section 9.2.5)
d) Analysis of blanks (Section 9.3.1)
e) Accuracy assessment (Section 9.5)
f) Ongoing precision and recovery (Section 9.3.2)

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (weight or other signal) to the final result. These data are to include :

a) Sample numbers and other identifiers
b) Digestion dates
c) Analysis dates and times
d) Analysis sequence/run chronology
e) Sample weight or volume
f) Digest volume
g) Make and model of DPASV instrument and standards traceable to NIST
h) Copies of log books, printer tapes and other recordings of raw data.
i) Data system outputs, and other data to link the raw data to the results reported

9.1.3 Analyses of laboratory blanks are required to demonstrate freedom from contamination. The procedure and criteria for analysis of a blank are described in Section 9.3.1.

9.1.4 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control These procedures are described in Section 9.4 and 9.3.2, respectively.

9.1.5 Analysis of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Section 9.5.

9.1.6 The laboratory should maintain records to define the quality of the data that is generated. Development of accuracy statements is described in Sections 9.3.2.3 and 9.5.9.

9.2 Initial demonstration of performance

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS), laboratory performance (determination of MDLs) and precision and recovery (determination of mean and standard deviation of replicate analyses) prior to performing analysis by this method.

9.2.2 Linear calibration range (LCR). The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use a minimum of a calibration blank and three calibration standards

If any verification data exceeds the initial values by ± 10%, linearity must be re-established. If any portion of the range is shown to be non-linear, sufficient standards must be used to clearly define the non-linear portion.

9.2.3 Quality control sample (QCS) Obtain a standard containing a known concentration of lead from a commercial source, different from the source of the CAL standards. Prepare a QCS with a concentration in the mid-range of the calibration (30 to 70 µg/L lead) by diluting the standard with reagent water or blank matrix. The QCS must be analyzed when beginning to use the method, on a quarterly basis, or as required to meet data-quality needs, and verify the calibration standards and acceptable instrument performance If the determined concentrations are not within ± 10% of the stated values, performance of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method detection limit (MDL). MDLs must be established for all analyses, using reagent water fortified at a concentration of one to five times the estimated instrument detection limit (Reference 16 6) To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method Perform all calculations defined in the method and report the concentration values in the appropriate units Calculate the MDL as follows

$$MDL = (t) \times (s)$$

Where t = Student's 't value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3 14 for seven replicates].

s = Standard deviation of the replicate analyses

MDLs should be determined every six months, when a new operator begins work, or whenever there is a significant change in the background or instrument response

9.2.5 Initial precision and recovery (percent recovery) To establish the ability to generate acceptable precision and accuracy, the analyst should perform the following operations :

9.2.5.1 Prepare a precision and recovery standard (PAR) by fortifying an LRB with QCS solution to a lead concentration of 30 to 70 µg/L Pb. Analyze four aliquots of the PAR according to the procedure in Section 11 0

9.2.5.2 Calculate the percent recovery of the added analyte for each observation, using the following equation :

Equation 1

$$R = \frac{C_a - C}{S} \times 100$$

where R = *Percent recovery (%)*
C_a = *Fortified blank concentration (µg/L)*
C = *LRB background concentration (µg/L)*
S = *Concentration equivalent of analyte added to the LRB (µg/L)*

9.2.5.3 Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation of the percent recoveries (s). Use the following equation for calculation of the standard deviation of the percent recovery :

Equation 2

$$s = \sqrt{\frac{\sum_{i=1}^{n} R_i^2 - \frac{\left(\sum_{i=1}^{n} R_i\right)^2}{n}}{n-1}}$$

where n = *number of samples*
R_i = *percent recovery in each sample (Reference 16.6)*

9.2.5.4 Compare s and X with the corresponding limits for initial precision and recovery in Section 17.0 (Table 1). If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem and repeat the test.

9.3 Assessing continuing laboratory performance

9.3.1 Laboratory reagent blank (LRB). The laboratory must analyze at least one LRB with each analytical batch to demonstrate freedom from contamination. Perform a laboratory reagent blank by substituting DI water for the sample and carrying out the full analytical procedure as described in Section 11.0. Data produced is used to assess contamination from the laboratory environment. Values that exceed the minimum level (Section 1.6) indicate that laboratory or reagent contamination should be suspected. Analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All sample must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.3.2 Ongoing precision and recovery (OPR). To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained, the laboratory must analyze at least one PAR with each batch of samples. The lead concentration of the PAR should be in the mid-range of the calibration (30 to 70 µg/L lead).

9.3.2.1 Calculate accuracy as percent recovery (Section 9.2.5.2). If the recovery of the analyte falls outside the required control limits of 80 to 120%, the analytical process is not in control. In this event, identify and correct the problem before repeating the OPR and analysis of the sample batch.

9.3.2.2 Development of criteria for evaluation of ongoing precision and recovery. When sufficient internal performance data is available (at least 20 to 30 analyses) optional control limits can be developed from 'X', the average percent recovery, and 's', the standard deviation of the individual percent recoveries. The data can be used to establish the upper and lower control limits as follows :

Upper control limit = X + 3s
Lower control limit = X - 3s

The optional control limits must be equal to or better than the required control limits of 80 to 120%

9.3.2.3 The laboratory should add results that pass the specification in Section 9.3.2.1 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality from X and s, expressing the accuracy as a recovery interval from X - 2s to X + 2s

9.4 Calibration verification. The laboratory must analyze at least one QCS and calibration blank daily to verify the calibration (Section 9 2 3). If the determined concentration is not within ± 10% of calibration, reanalyze the QCS If the second analysis confirms the calibration is outside the limits, halt sample analysis and determine the cause. In the case of drift, recalibrate the instruments. All samples following the last acceptable QCS must be reanalyzed. The analysis data of the QCS and calibration blank must be kept on file with the sample analyses data.

9.5 **Assessing analyte recovery and data quality matrix spikes.**

The laboratory must spike, in duplicate, a minimum of 10 percent of all samples from a given sampling site The two sample aliquots shall be spiked with lead solution (Section 7.8.1).

9.5.1 The spiking level shall be high enough to be detected above the original sample and should not be less than four times the MDL. It should, preferably, be one to five times the action level for lead (15 µg/L).

9.5.2 Using the independent lead standard, prepare the spiking solution of 5000 µg/L lead. Using a 100-mL aliquot of sample, 1.0-mL of spiking solution fortifies the sample by 50 µg/L lead

9.5.3 Analyze one sample aliquot according to the procedure in Section 11 to determine the background concentration of lead (C).

9.5.4 Spike two further sample aliquots (MS and MSD) with the spiking solution and analyze these aliquots to determine the concentration after spiking (C_s), using the procedure in Section 11.

9.5.5 Calculate the percent recovery, R, of lead in each aliquot using the following equation :

Equation 3

$$R = \frac{100\,(C_s - C)}{T}$$

where.

R = *Percent recovery*
C_s = *Measure concentration of analyte after spiking*
C = *Measured background concentration*
T = *True concentration of the spike*

9.5.6 Compare the percent recovery with the corresponding QC acceptance criteria in Section 17.0 (Table 1)

9.5.6.1 If the recovery of the spike fails the acceptable criteria, and the recovery of the QC standard in the OPR test (Section 9.3.2) for the analytical batch is within the acceptable criteria in Table 1, an interference is present. If the interference is attributable to sampling, the site should be resampled. If the interference is attributable to method deficiency, the analyst must modify the method, repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS/MSD

9.5.6.2 If the results of both the spike and the OPR fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample reanalyzed

9.5.7 Compute the relative percent difference (RPD) between the two results (not between the two recoveries) using the following equation:

Equation 4

$$RPD = \frac{(D_1 - D_2)}{0.5\,(D_1 + D_2)} \times 100$$

where

D_1 = *Measure concentration of lead in aliquot one (MS)*
D_2 = *Measured concentration of lead in aliquot two (MSD)*

9.5.8 The relative percent difference for duplicates shall meet the acceptance criteria in Table 1. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch reanalyzed.

9.5.9 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained. After the analysis of five spiked samples in which the recovery passes the test in Section 9.5.6, compute the average percent recovery (Pa) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from Pa - $2s_p$ to Pa + $2s_p$. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.6 The specifications contained in this method can be met if the apparatus used is scrupulously cleaned. The standards used for initial precision and recovery (IPR Section 9.2.5), ongoing precision and recovery (OPR Section 9.3.2), and matrix spikes (MS/MSD Section 9.5), should be identical, so that the most precise results will be obtained.

9.7 Depending upon specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration and Standardization

10.1 Prepare a series of at least three CALs and a CB covering the desired concentration range, by diluting suitable volumes of ISS (7.7.1) with DI water.

10.2 Process CALs and CBs as described in Section 11.0, Procedure.

10.3 Prepare a standard curve by plotting instrument response against concentration values. The calibration curve may be derived using manual plotting or computer- or calculator-based regression curve fitting techniques.

10.4 After the calibration has been established, it should be verified with a ACS as described in Section 9.4.

10.5 Calibration standards shall be within ± 10% at 15 µg/L and 60 µg/L. If the calibration standards are not within these limits, consult the equipment manufacturer.

11.0 PROCEDURE

11.1 **Preparation of standard solution.** Neutralize to above pH 4.0 with a minimum volume of sodium hydroxide. Take 50-mL of standard in a sample container, add two drops of methyl orange indicator solution (Section 7.2) and add 1.5M sodium hydroxide solution dropwise until the colour changes from pink to yellow. Analyze the neutralized standard immediately.

11.2 **Sample preparation for dissolved lead.** Neutralize the filtrate to above pH 4.0 with a minimum volume of sodium hydroxide. Take 50-mL of sample in a sample container, add two drops of methyl orange indicator solution (Section 7.2) and add 1.5M sodium hydroxide solution drop wise until the colour changes from pink to yellow. Analyze the neutralized sample immediately.

Note: *The use of a pH meter to monitor the neutralization process has been found to introduce unacceptable levels of contamination.*

11.3 **Sample preparation for total recoverable lead.** Acid digestion must be carried out. Take a 100-mL (± 1-mL) aliquot from a well-mixed, acid preserved sample and transfer it to a 250-mL conical beaker. Add 1 mL of concentrated nitric acid and 0.5 mL of concentrated hydrochloric acid. Heat the sample on a hot plate at 85°C until the volume has been reduced to approximately 20 mL, ensuring that the sample does not boil.

Note: *For proper heating, adjust the temperature control of the hot plate such that an uncovered beaker containing 50 mL of water located in the center of the hot plate can be maintained at approximately, but no higher than, 85°C. Evaporation time for 100 mL of sample at 85°C is approximately two hours with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL.*

Cover the beaker with a watch glass and reflux for 30 minutes. Slight boiling may occur but vigorous boiling should be avoided. Allow to cool and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume with DI water and mix.

Neutralize the acid digest to above pH 4.0, with a minimum volume of sodium hydroxide solution. Take 50 mL digested sample in a sample container, add two drops of methyl orange indicator solution (Section 7.2) and add 6.0M sodium hydroxide solution drop wise until the color changes from pink to yellow. Analyze the neutralized sample immediately.

11.4 Dispense 5 mL of prepared sample to the 5-mL plastic tube provided and proceed immediately.

11.5 Add one Conditioning tablet (Section 7.5) to the 5 mL of sample. Crush tablet with a crushing rod and mix to dissolve. Ensure the tablet is completely dissolved.

11.6 Place the instrument on a clean, dry surface, in an environment free from dust, draughts, and vibration, within the temperature range 20 to 25°C. Insert the tube of prepared sample into the test tube holder.

11.7 Press the 'ON' key. The instrument display shows the calibration code. Compare this number with the code on the sensor packaging. Press 'ENTER' to accept, or key in the correct code and press 'ENTER'.

Note: *Check the expiry date on the sensor packaging. Do not use expired sensors.*

11.8 The instrument proceeds with an automatic system and battery check, and will not allow analysis unless these are satisfactory.

11.9 At the screen prompt 'Insert electrode and immerse' take one disposable sensor (Section 7.6) and open the foil strip. Insert the sensor tracks into the connector cap and immerse the sensor into the sample. Do not disturb the instrument or sample during the test.

11.10 The instrument senses the sample and automatically begins the analysis. After three minutes the results appear on-screen as a direct reading.

11.11 Depress the button on the connector cap to eject the used sensor.

Note: *The instrument is programmed to recognize a number of user errors, such as used or contaminated sensors, poor electrical connection or failure to add conditioning tablet The instrument will abort the test and display an error message. It is important to keep the connector cap clean and dry to avoid repeated error messages due to wet or dirty electrical contacts*

12.0 Data Analysis and Calculations

12.1 If a sample dilution has been used, multiply the answer by the appropriate dilution factor

Equation 5

$$\text{Dilution Factor} = \frac{\text{Total Volume}}{\text{Sample Volume}}$$

where

Sample Volume = *Aliquot of sample taken for dilution (mL)*
Total Volume = *Volume to which sample volume is diluted (mL)*
Corrected Concentration = *Observed concentration x dilution factor*

12.2 Reporting

12.2.1 Report results in micrograms per liter (µg/L Pb).

12.2.2 Report results to two significant figures above 10 µg/L. Report results to one significant figure below 10 µg/L.

12.2.3 Report results below the ML as less than the ML (Section 1.5).

13.0 Method Performance

13.1 Using the Palintest Scanning Analyzer SA-1000, the standard deviation of replicate observations (n = 10) of a calibration standard containing 15 µg/L lead was 0 75 µg/L.

13.2 With multiple batches of tablet reagents and sensors, the relative standard deviation of sets of observations (n = 10) of a calibration standard containing 15 µg/L lead varied from 2.1 to 3.8%.

13.3 A single laboratory reported the analysis of seven aliquots of a drinking water sample, initially containing 8 µg/L lead, but fortified to a total lead concentration of 48 µg/L The mean percent recovery of the added 40 µg/L lead was 110% and the corresponding standard deviation of the percent recoveries was 1.5%

14.0 Pollution Prevention

14.1 The quantity of chemical purchased should be based on expected usage during its shelf-life and disposal cost of unused material.

14.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required

15.2 Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner The MSDS sheet gives details of product composition and may be consulted for guidance on waste disposal

15.3 Samples preserved with nitric acid to pH <2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste

15.4 Standards containing lead must be handled as hazardous waste

15.5 For further information on waste management, consult "The Water Management Manual for Laboratory Personnel", and "Less is Better Laboratory Chemical Management for Waste Reduction", both available from the American chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N W , Washington DC. 20036

16.0 References

16.1 "Carcinogens-Working With Carcinogens", Department of Health, Education, and Welfare. Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No 77-206, August 1977

16.2 "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976)

16.3 "Safety in Academic Chemistry Laboratories", American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979

16.4 D1193-91 Standard Specification for Reagent Water Annual Book of ASTM Standards. Volume 11.01, Philadelphia PA American Society of Testing Materials 1993

16.5 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories", USEPA, EMSL-Ci, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

16.6 Code of Federal Regulations. Title 40, Part 136, Appendix B

17.0 Tables and Graphs

17.1 Table 1 Acceptance Criteria for Performance Tests

Acceptance Criterion	Section	Limit (%)
Initial precision and recovery		
Precision (s)	9.2 5.4	5
Recovery (X)	9.2.5 4	80-120
Ongoing precision and recovery		
Recovery (X)	9 3 2.1	80-120
Calibration verification		
QCS Recovery	9.4	90-110
Matrix spike/matrix spike duplicate		
Recovery	9.5.6	80-120
Precision (relative percent difference)	9 5 8	20

17.2 Graph 1 Example calibration graph