HANDBOOK FOR THE DEPARTMENT OF ENERGY'S MIXED ANALYTE PERFORMANCE EVALUATION PROGRAM (MAPEP)

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It is the Radiological and Environmental Sciences Laboratory's (RESL) policy to conduct business in accordance with all applicable U.S. export control laws and regulations. It is also RESL's policy that its Customers comply with U.S. export control laws and regulations. Therefore, the Customer agrees to the following:

1. Because products, technical data, and technical assistance (i.e., services) provided to the Customer by RESL may be subject to U.S. export control laws and regulations, (i) transactions with certain persons and companies and (ii) the export or re-export of certain types and levels of products, technical data, and services are prohibited or restricted. These laws include, without limitation, the Arms Export Control Act, the Export Administration Act, the International Emergency Economic Powers Act, and the Atomic Energy Act and regulations issued pursuant to these, including, without limitation, the Export Administration Regulations (EAR) (15 CFR Parts 730-774), the International Traffic in Arms Regulations (ITAR) (22 CFR Parts 120-130), the Foreign Assets Control Regulations (31 CFR Parts 500-598), and the Nuclear Regulatory Commission and Department of Energy export regulations (10 CFR Parts 110 and 810).

2. Customer acknowledges that they are responsible for their own compliance with U.S. export control laws and regulations. The Customer further agrees that they assume the responsibility to obtain all necessary U.S. export licenses or other U.S. governmental authorizations, as well as all liability for the failure to do so.

3. Customer acknowledges that export control requirements may change and that the export or re-export of RESL products, technical data, and services without an export license or other appropriate governmental authorization may result in criminal and/or civil liability. The Customer further acknowledges that they can contact the U.S. Departments of Commerce, Energy, State, and Treasury, as well as the U.S. Nuclear Regulatory Commission, for guidance as to applicable licensing requirements and other restrictions.

4. The obligations and requirements described herein shall survive the expiration or termination of any agreement or contract between RESL and the Customer.

I. INTRODUCTION

Compliance and quality assurance issues associated with the Department of Energy (DOE) environmental programs typically require analytical services under contract with DOE to participate in a variety of proficiency testing programs (PTPs). The primary objective of the PTPs is to foster reliability and credibility for the analytical results used in the decision-making process, particularly for those decisions affecting the environment, public health, and safety. Each PTP checks for specific analytical proficiencies in radiological or stable inorganic analyses. The proficiency testing (PT) standards used to test analytical proficiencies, however, often do not resemble the real-world environmental samples analyzed for DOE. PT standards are frequently prepared with only a few target analytes in a concentrated or purified sample matrix, such as deionized or distilled water, with little chemical or other interferences. In comparison, the environmental samples submitted for routine analysis typically have multiple target analytes in a whole-volume, non-concentrated and non-purified, natural matrix with numerous chemical or other interferences. Additionally, since the PT material is prepared for either radiological or stable inorganic analyses, the combined analytes are not in the same PT standard. Yet, the environmental samples analyzed for DOE typically contain a mixture of constituents from each analytical category. Regulatory requirements frequently include analyses of radiological and non-radiological constituents (i.e., "mixed analytes") from the same environmental sample. Thus, DOE clearly needs PT material that contains mixed analytes in the same real-world sample matrix for testing the analytical proficiency of contracted services. A mixed analyte PTP, however, was previously not available. The Analytical Services Division of the DOE-HQ Office of Environmental Management (EM) established the MAPEP in 1994 to address this deficiency and to help assure the quality of analytical services across the DOE Complex.

The Radiological and Environmental Sciences Laboratory (RESL) shall administer the MAPEP. MAPEP standards, distributed twice a year, include mixed analyte water and soil matrices with environmentally important radiological and stable inorganic constituents. Water and soil are typically among the most important matrices for DOE analytical services. Radiological air filter and vegetation matrices, and gross alpha/beta standards for water and air filter matrices, are also provided. Consolidating the major analytes of interest into a single PT sample provides a more representative mixed analyte standard for the water and soil matrices and an efficient means for laboratories to demonstrate required proficiencies. The radiological vegetation and air filter standards address the quality assurance needs of DOE radiological programs, environmental monitoring, and long-term stewardship. MAPEP currently offers synthetic urine and synthetic fecal standards, which provide labs the opportunity to measure and evaluate the effectiveness of their direct radiobioassay procedures. The special radiological matrix (XrM) provides difficult sample matrices and various radionuclides to challenge analytical capabilities and encourage participation without the concerns associated with a potentially poor performance. MAPEP provides real-world, whole volume PT samples with known specific activities or concentrations and is designed to evaluate and improve the analytical performance of environmental laboratories across the DOE complex.

II. PARTICIPATION

All laboratories that perform environmental analytical measurements for DOE (i.e., radiological,

stable inorganic, solely or in any combination) are required to participate in the MAPEP (Memorandum from the Assistant Secretary for Environmental Management, May 31, 1994, Newberry: 3-7615). In addition to the 1994 memorandum, a Memorandum from the Chief Health, Safety and Security Officer, Glenn Podonsky, dated December 30, 2013 emphasizes, "To ensure high-quality, defensible data, it is recommended that all onsite and subcontracted environmental laboratories performing radiological, inorganic or organic analysis for DOE be encouraged to participate in the Mixed Analyte Performance Evaluation Program (MAPEP)." It is important to note that MAPEP PT standards are a mixed analyte reference material, not a mixed waste: "MAPEP standards are analytical standards or a product generated for the purpose of securing and evaluating analytical services; they are not hazardous waste and they are not samples of hazardous waste... Thus, a laboratory participating in the MAPEP is in the process of establishing its eligibility and credentials to do DOE analytical work." (Memorandum OCC-95-189, Office of the Chief Council, October 16, 1995). Successful participation is defined as requesting the PT standards, completing the appropriate analyses, reporting the results to RESL, receiving acceptable performance as defined by MAPEP.

MAPEP participation may be requested by emailing a request to DOEIDmapep@id.doe.gov. MAPEP applications are also available under the MAPEP program information link on the RESL public website at https://resl.id.energy.gov/MAPEP/mapep.html or the secure, password-protected MAPEP website at https://mapep.inl.gov/. A request for participation should include a shipping and correspondence address, a contact person for each, appropriate phone numbers, e-mail address, any special shipping instructions, the current NRC or state license number for the laboratory or a statement of NRC license exemption, and the license or exemption expiration date. MAPEP standards cannot be shipped to a post office box. Since the MAPEP standards have a radioactive component, an NRC license or exemption is required for the receiving laboratories. Exemptions should specify the DOE contract number for the laboratory.

Participating laboratories are required to have appropriate radiological control measures. Furthermore, in performing sample analyses the participating laboratory accepts title and ownership of the MAPEP standard and becomes the generator of any resulting waste or sample residues.

III. ACCREDITATION

Certificates of MAPEP Accreditation of Analytical Performance are issued to those participants whose analytical performance capabilities have been evaluated and have successfully demonstrated accurate analytical results on real world samples of interest to DOE.

Requisites for the Certificates of MAPEP Accreditation of Analytical Performance include completing the MAPEP test session as specified, successfully reporting accuracy, sensitivity, and false positive/negative testing in the various PT sample matrices.

IV. SAMPLE PREPARATION, CHARCTERIZATION, AND VERIFICATION

Liquid MAPEP standards are prepared from radiological and stable inorganic standards that are traceable to the National Institute of Standards and Technology (NIST). Final concentrations for these analytes are calculated from the NIST certified standard value and the standard dilution(s) used. A known quantity of standard is combined and diluted to a known final volume with 7-10%

(v/v) nitric acid and characterized natural ground or surface water. All sample containers are polyethylene or glass bottles.

Solid standards are prepared from natural soil matrices spiked with NIST traceable standards for the various analytes of interest. The PT standard is characterized, homogeneity is assessed, and target analyte concentrations are verified prior to sample distribution. Known values for the radiological and stable inorganic analytes are calculated from the NIST certified standard values and the standard dilution(s) used. Rarely, a known value is derived from the sample characterizations. Sample handling and storage procedures are similar to those for the liquid PT standard. Appendix F delineates the requirements for MAPEP PT standards material preparation and verification in accordance with the requirements of ISO/IEC 17025, ISO/IEC 17043, and ISO 17034.

The U.S. Department of Transportation (DOT) does not typically classify MAPEP standards as radioactive. Participants are provided PT standard descriptions that delineate the major analytes of interest, concentration ranges, and other important sample information. Each participant is responsible for determining if the analytical procedures used to analyze the MAPEP standards generate mixed waste. Analyses must not proceed without full compliance to all applicable regulatory authorities.

V. SAMPLE DISTRIBUTION

Standards are distributed biannually. Sample descriptions and instructions will be available on the Internet prior to each sample distribution. Current Sample Descriptions can be found on the RESL public website at https://resl.id.energy.gov/MAPEP/describe.html for all MAPEP proficiency testing matrices. The MAPEP must be notified of any special shipping requirements prior to distribution. Participants must ensure they are authorized to receive a MAPEP sample and that their standard operating procedures incorporate appropriate sample management and waste disposal practices. Acceptance of the MAPEP sample(s) means the participating laboratory takes title and ownership of the sample(s). Excess sample or associated residues cannot be returned to RESL. Sample analysis shall not be initiated if approved treatment, storage, or disposal options are not available.

VI. SAMPLE ANALYSES

Analyses are required for only those analytes that are a component of the participant's routine analytical workload or compliance requirements (i.e., a complete analysis of the sample may not be required). Laboratories must report results for a targeted analyte if the determination is typically given by the analytical methodology utilized. For example, if Pu-238 and Pu-239 are targeted analytes, and results for Pu-239 are reported utilizing alpha spectrometry, the results for Pu-238 must also be reported. The same analytical procedures employed for routine analyses should also be utilized for MAPEP standards. MAPEP, however, may also be used to develop new analytical methods or demonstrate proof of process. Participants are typically allowed 60 calendar days to complete those analyses not controlled by regulatory holding times. The deadline for reporting results is specified for each sample distribution.

Although analytical methods are not prescribed by MAPEP, standard analytical procedures will be utilized to independently characterize and verify the MAPEP standards. These analytical techniques include alpha spectrometry, beta counting, gamma spectrometry, inductively coupled plasma (ICP) atomic emission spectroscopy, ICP mass spectrometry, gas chromatography, gas chromatography/mass spectrometry, and other common analytical methods.

Activities for radiological analytes are typically sufficient to provide a 5-10% counting uncertainty with a reasonable sample size and count time. Similar uncertainties should be achievable for most stable inorganic analytes. The amount of sample is, however, limited. Therefore, the activity and concentration ranges indicated in the sample description must be used to select the optimum quantity of sample for each analysis.

VII. REPORTING RESULTS

Analytical results are reported to RESL electronically. Data entry and edit screens are available for reporting the analytical results via the Internet; a hard copy record can be printed for laboratory records or review. Data entry and editing is allowed any time prior to the closing date of the particular study. The data entry program guides the user through selection of Method Codes for radiological (see Appendix B) and stable inorganic (see Appendix C) analyses. Data are entered directly into the MAPEP database via the MAPEP website. Specific instructions for using the data entry program are provided in Appendix E.

The MAPEP will not accept hard copy results or data sent by email, or other electronic media, without prior authorization. MAPEP participants must adhere to RESL and MAPEP policies, including the acknowledgement of MAPEP website notices, submitting periodic Site User Agreements, and compliance with U.S. export control laws and regulations. MAPEP participants must respond in a timely manner to MAPEP requests and keep their laboratory contact information current. Failure to adhere to these expectations may result in suspension of MAPEP participation.

Participants are required to report only one result for each appropriate analyte. Each reported radiological and inorganic result must be accompanied by an estimate of its uncertainty in the units of measurement (not as a percent), and both numbers should follow the rules for significant figures. Do not report a zero (0.0) result or uncertainty. If the reported result is a mean of several replicate analyses, the reported uncertainty should also be the mean of the individual uncertainties at one standard deviation. Do not combine the variances associated with the individual uncertainties for replicate measurements, even though this should typically be performed. The larger individual uncertainties associated with a single analysis are of interest to MAPEP since they are more indicative of routine performance. For example, assume three replicate analyses provided the following results and individual uncertainties: 101 +/- 12, 108 +/- 15, and 110 +/- 16. The mean result is (101+108+110)/3=106 and the mean individual uncertainty is (12+15+16)/3=14. The result and total uncertainty as reported for MAPEP is 106 +/- 14. The total uncertainty is reported at one standard deviation.

The uncertainty characterizes the range about the result within which the true value is expected to lie (result +/- uncertainty). The uncertainty provides a probabilistic statement about the extent to which the result may be inaccurate. Because of Poisson counting statistics, a unique uncertainty can be propagated for each radiological result. This is not necessarily the case for stable element

analyses where average uncertainties may be assigned for different analytes and concentration ranges. The exact method for estimating the uncertainty is not prescribed here since the reported uncertainty for MAPEP analyses should reflect the actual methods used for data generated on routine real-world samples. For guidance, however, it is preferred to estimate all uncertainty components, including those derived from a complete statistical analysis (Type A, s_A) and those evaluated by other means (Type B, s_B), as approximations to standard deviations. This convention follows that proposed by the Bureau International des Poids et Mesures (BIPM) and as suggested in several standard references (NIST Technical Note 1297, 1994; ISO/IEC/OIML/BIPM *Guide to the Expression of Uncertainty in Measurement*, 1995; NCSL Information Manual - *Determining and Reporting Measurement Uncertainties*, RP-12, 1994; ANSI/NCSL Z540-2-1997 *American National Standard for Expressing Uncertainty--U.S. Guide to the Expression of Uncertainty in Measurement*; A2LA G104 *Guide for Estimation of Measurement Uncertainty in Testing*, 2014; ANSI N42.14-1999 *Calibration and Use of Germanium Spectrometers for the Measurement of Gamma-Ray Emission Rates of Radionuclides*; NCRP Report No. 58, second edition, 1985). It allows all of the uncertainty components to be propagated into a total combined uncertainty by statistical rules and the combination of variances:

$$u = \sqrt{s_A^2 + s_B^2}$$

where u = the combined uncertainty and the other variables are as described above.

For example, let R = the analytical result, ΔR = the total combined uncertainty in the result.; let U1 = an uncertainty component involved in the calculation of the result (such as a pipette calibration), ΔU1 = the uncertainty in the pipette calibration derived statistically as the standard deviation of 10 measurements, i.e., an example of Type A uncertainty; let U2 = a second uncertainty component, such as the value of a calibration standard used in calculating the result, ΔU2 = the uncertainty of the calibration standard obtained from a standard certificate at one standard deviation, i.e., an example of Type B uncertainty; let U3 = a third uncertainty component, such as a weight measurement, ΔU3 = the uncertainty in the weight measurement; let U4 = a fourth uncertainty component, such as a volume measurement, ΔU4 = the uncertainty in the volume measurement, etc. Note that all uncertainty components, including Type B uncertainty, should be estimated at one standard deviation. The equation used to calculate the total combined uncertainty in the result is given by:

$$\Delta R = R * \sqrt{[\frac{\Delta U1}{U1}]^2 + [\frac{\Delta U2}{U2}]^2 + [\frac{\Delta U3}{U3}]^2 + [\frac{\Delta U4}{U4}]^2 + ...}$$

This example is for illustrative purposes only; frequently the uncertainty components cannot be derived directly but must rely on the mathematical manipulation of other measurable quantities. In this event, the specific error propagation formulas for the various mathematical functions, i.e., addition, subtraction, multiplication, division, exponential, etc., must be utilized. These formulas and a detailed discussion on error propagation can be found in the references cited above and other statistical and analytical references.

It is important to report all uncertainties at one standard deviation in the units of measurement, not in percent. Many MAPEP participants utilize EPA methodology and therefore may not routinely report uncertainties. The MAPEP, however, stresses the importance of determining the uncertainty of a measurement as outlined in the ISO/IEC, NIST, and other references cited above. Understanding the uncertainty of measurements is crucial for quality control and the improvement of radiological and stable inorganic analytical methods.

Laboratories must not report a result for those components that are not routinely analyzed (i.e., leave blank). Failure to follow this rule may result in inappropriately derived performance flags for a target analyte.

VIII. PERFORMANCE EVALUATION

Acceptance criteria for MAPEP were developed from a review of precision and accuracy data compiled by other PTPs, the analytical methods literature, from several MAPEP pilot studies, and from what is considered reasonable, acceptable, and achievable for routine analyses among the more experienced laboratories. The acceptance criteria are designed to be pragmatic in approach and may be changed as warranted. The typical performance evaluation methods and acceptance criteria are identical for radiological and inorganic targeted analytes. All performance evaluations must have a minimum of six or more acceptable results for the targeted analyte before means are calculated and other statistical analyses are performed. The performance for analytes with less than six acceptable results is not evaluated.

1) **For each reported radiological and stable inorganic analyte**, the laboratory result and the RESL reference value is used to calculate a relative bias:

$$\%\ BIAS = \frac{(100)(Laboratory\ Result - RESL\ Reference\ Value)}{RESL\ Reference\ Value}$$

The relative bias places the laboratory result in one of three categories for the radiological and stable inorganic analytes:

1) ACCEPTABLE ..... $|BIAS| \leq 20\%$
2) ACCEPTABLE WITH WARNING ... $20\% < |BIAS| \leq 30\%$
3) NOT ACCEPTABLE ..... $|BIAS| > 30\%$

The performance evaluation associated with the special radiological matrix (XrM) tests the analytical capabilities of participants without placing acceptance limits on performance. The participants receive little information pertaining to the sample matrix and the targeted radionuclides so that the sample is largely unknown. Each reported XrM result will have the bias from the RESL known value calculated, but the reported results will not be flagged or evaluated by any acceptance criteria, i.e., the reported results will not be evaluated as "Acceptable", "Acceptable with Warning", or "Not Acceptable". Participants will see the bias of their reported result from the known and can evaluate their own performance. MAPEP will not issue Letters of Concern for any performance associated with the XrM sample. The goal is to allow participants to test their capabilities on a variety of unknown sample matrices and analytes without the fear and potential negative ramifications that may result from a poor performance evaluation.

2) **Radiological and stable inorganic analyte uncertainty evaluation.** Radiological and inorganic results must be reported with an associated uncertainty at one standard deviation. The reported uncertainty associated with a result is not currently used as part of the acceptance criteria, but an uncertainty evaluation will be used to flag potential areas of concern. Activity levels and other analyte concentrations for MAPEP standards are typically sufficient to permit analyses with uncertainties of 5-10% or less, but it is unreasonable to expect the uncertainty for a single analysis of a routine sample to be much lower than the 5-10% value. Variations in counting efficiencies, chemical yields, analytical methods, sample size, count times, difficult analyses, etc., will likely cause some uncertainties to exceed the 5-10% value. A meaningful routine analysis, however, will not over inflate the uncertainty estimate. The MAPEP will provide some feedback to the participants regarding the uncertainties reported with their results. Reported total uncertainties that appear unreasonably low or suspiciously high will be flagged as potential areas of concern.

MAPEP will assign radiological and stable inorganic uncertainty flags A for "Acceptable", W for "Acceptable with Warning", and N for "Not Acceptable". Relative precision (RP) is defined as the ratio of the precision of a given measurement and the value of the measurement itself, expressed as a percent: *RP = (Reported Uncertainty / Reported Result) x 100.* The uncertainty flag criteria are:

1) NOT ACCEPTABLE ..... RP < 2%
2) ACCEPTABLE ……..... 2% ≤ RP ≤ 15%
3) ACCEPTABLE WITH WARNING... 15% < RP ≤ 30%
4) NOT ACCEPTABLE ..... RP > 30%

The uncertainty flags are currently for information only, but reported total uncertainties are used to evaluate performance in false positive/negative tests and sensitivity evaluations (see Appendix F). False positive results are a very important quality concern for DOE since they typically initiate needless investigations, require additional sampling and analysis, and are used to formulate erroneous decisions, thereby increasing DOE's liability risk and taxpayer costs.

IX. PERFORMANCE REPORTS

Participants will receive email notification when their respective performance reports are available for review. The participant's report will include the RESL reference value for the analyte of interest, the laboratory reported value, acceptance status, and the grand mean for all laboratories.

Other pertinent or helpful information may also be included where necessary. MAPEP participants will not be scored or ranked. The performance of each laboratory will be monitored, and corrective actions may be called for as required where necessary. MAPEP routinely issues Letters of Concern to highlight potential quality issues. It is MAPEP's intent to inform each laboratory of potential quality concerns revealed by MAPEP participation. It is the responsibility of each laboratory to investigate their consistent "NOT ACCEPTABLE" or "ACCEPTABLE with WARNING" performance evaluations. Each notified laboratory should determine the cause(s) for the identified quality concern and make the appropriate procedural changes necessary to improve future data quality.

X. COMMUNICATION WITH MAPEP PARTICIPANTS AND STAKEHOLDERS

MAPEP communicates with participants and stakeholders primarily with notifications from email and information posted on the MAPEP websites. The communications include routinely scheduled items for each test session, such as enrollment periods, PT sample selection(s), shipping dates, closing dates, sample descriptions, test session instructions, individual performance reports, final PT reports, and Letters of Concern. Performance evaluation reports and program information are provided on the secure password-protected MAPEP website at https://mapep.inl.gov/ and later on the RESL public website at https://resl.id.energy.gov/MAPEP/mapepreports.html. MAPEP participants and stakeholders may use the secure MAPEP password-protected website. The secure website provides several database tools for generating various reports, tracking and trending historical performance and other helpful resources. The secure website is also where participants receive the MAPEP Letters of Concern regarding potential quality issues.

XI. CRITERIA FOR LETTERS OF CONCERN

The following information provides a brief overview of the policies and processes associated with issuing and responding to a MAPEP Letter of Concern.

The MAPEP issues a Letter of Concern to a participating laboratory upon identification of a potential analytical data quality problem in the MAPEP results in order to help participants identify, investigate, and resolve potential quality issues. Letters of Concern have been issued since 1996, shortly after the beginning of the MAPEP program. A copy of the Letter of Concern is also available for the DOE stakeholders. Issued to be informative and not punitive, each Letter of Concern states, "*This letter is solely intended to alert your laboratory to a potential quality concern that you may wish to investigate for corrective action*." A Letter of Concern is issued to any participating laboratory that demonstrates:

> "Not Acceptable" performance for a targeted analyte in a given sample matrix for the two most recent test sessions (e.g., Pu-238 in soil test 13 "+N" (+36% bias), Pu-238 in soil test 14 "-N" (-43% bias));
>
> "Not Acceptable" performance for a targeted analyte in two or more sample matrices for the current test session (e.g., Cs-137 in water test 14 "+N" (+38%), Cs-137 in soil test 14 "+N" (+45%));
>
> Consistent bias, either positive or negative, at the "Warning" level (greater than ±20% bias)

for a targeted analyte in a given sample matrix for the two most recent test sessions (e.g., Sr-90 in air filter test 13 "+W" (+26%), Sr-90 in air filter test 14 "+W" (+28%));

Quality issues (flags other than "Acceptable") that weren't identified by the above criteria for a targeted analyte in a given sample matrix over the last three test sessions (e.g., Am-241 in soil test 12 "-N" (-47%), Am-241 in soil test 13 "+W" (+24%), Am-241 in soil test 14 "-N" (-38%));

Any other performance indicator and/or historical trending that demonstrate an obvious quality concern (e.g., consistent "False Positive" results for Pu-238 in all tested matrices over the last three test sessions).

A review period of about two weeks is provided at the close of each MAPEP test session prior to the release of final results to DOE stakeholders and the general public. Any participating laboratory may question or appeal performance evaluation results during this review period. All laboratories may respond to a Letter of Concern by contacting MAPEP, and many frequently do so. Laboratories can also request additional MAPEP standards at any time for verification of measurement processes, and many have utilized this option.

In addition to issuing Letters of Concern, the MAPEP Team provides technical assistance whenever requested, to both MAPEP participants and DOE/contractor oversight personnel. MAPEP Letters of Concern are instrumental in this process by providing a method of communication that focuses attention on analytical performance. When used as intended, the MAPEP Letters of Concern assist laboratories and DOE/contractor oversight personnel avoid potential quality problems and correct quality issues in a timely manner.

It is important to note that MAPEP is a proficiency-testing program, not an enforcement organization. MAPEP can identify potential quality concerns, but MAPEP does not issue or enforce corrective actions. The majority of analytical services under contract with DOE rely on a DOE field organization or primary contractor for oversight of the analytical services. Therefore, DOE field management, DOE contractors, and oversight personnel are responsible to ensure analytical services contracted with DOE for providing environmental data meet their contractual obligations. They must confirm whether the corrective actions needed to remedy any data discrepancies identified by the MAPEP proficiency testing satisfy the commitments made to, and on behalf of, DOE. Confidence in the quality, validity, and reliability of the analytical data is dependent on this process.

APPENDIX A

List of MAPEP Target Analytes

Radiochemical Analytes

Actinium-228	Americium-241	Antimony-124
Antimony-125	Barium-133	Bismuth-212
Bismuth-214	Cadmium-109	Carbon-14
Cerium-139	Cerium-144	Cesium-134
Cesium-137	Cobalt-57	Cobalt-58
Cobalt-60	Curium-244	Europium-152
Europium-154	Europium-155	Hydrogen-3
Iodine-129	Iron-55	Iron-59
Lead-212	Lead-214	Manganese-54
Neptunium-237	Nickel-63	Plutonium-238
Plutonium-239/240	Plutonium-241	Polonium-210
Potassium-40	Protactinium-234m	Radium-226
Radium-228	Ruthenium-106	Selenium-75
Silver-110m	Strontium-89	Strontium-90
Sulfur-35	Technetium-99	Thallium-208
Thorium-227	Thorium-228	Thorium-230
Thorium-232	Tin-113	Uranium-234/233
Uranium-235	Uranium-238	Yttrium-88
Zinc-65	Zirconium-95	

APPENDIX A

List of MAPEP Target Analytes

Inorganic Analytes

Aluminum	Antimony	Arsenic
Barium	Beryllium	Cadmium
Calcium	Chromium	Cobalt
Copper	Iron	Lead
Magnesium	Manganese	Mercury
Molybdenum	Nickel	Potassium
Selenium	Silver	Sodium
Thallium	Uranium-Total	Uranium-235
Uranium-238	Vanadium	Zinc

APPENDIX B

Method Codes for Radionuclides

1. The first pair of digits designates the method of detection (instrument).

   00 Alpha Spectrometry
   01 Beta Counting - 2 pi gas flow proportional counter
   02 Beta Counting - liquid scintillation counter
   03 Gamma Spectrometry
   04 Gross Alpha/Beta - 2 pi gas flow proportional counter
   05 Thermal Ionization Mass Spectrometry
   07 Kinetic Phosphorescence Analyzer (KPA)
   08 Inductively Coupled Plasma Mass Spectrometry
   99 Other

2. The second pair of digits designates the sample preparation method.

   00 No preparation - analyzed as received
   01 Evaporation, straight
   02 Evaporation, acidified
   03 Coprecipitation, straight
   04 Coprecipitation, acidified
   05 Distillation
   06 Acid leaching without hydrofluoric acid
   07 Wet ash - Acid digestion - the use of oxidizers to destroy organics
   08 Acid dissolution by strong Aqua Regia, hydrofluoric acid, etc.
   09 Total dissolution by fusion
   10 Ion Exchange Chromatography / Ion Chromatography
   11 EPA 900, Radioactivity, Gross Alpha/Beta Screening, 600/4-80-032
   12 EPA 901, Radioactive Cesium, 600/4-80-032
   13 EPA 901.1, Gamma Emitting, 600/4-80-032
   14 EPA 905, Radioactive Strontium, 600/4-80-032
   15 EPA 906, Tritium, 600/4/80-032
   16 EPA 907, Actinide Elements, 600/4/80-032
   17 EPA 908, Uranium-Radiochemical Method, 600/4/80-032
   18 EPA 908.1, Uranium-Fluorometric Method, 600/4-80-032
   19 EPA 00-07 – Radiochemistry Procedures Manual
   20 SM7110C – Gross alpha and beta radioactivity
   99 Other

3. The final digit is a letter (A through G) indicating the sample size (see Appendix E).

APPENDIX C

Method Codes for Inorganic Metals

1. The first pair of digits designates the method of detection (instrument).

   00 Flame Atomic Absorption Spectrometry
   02 Radial - Inductively Coupled Plasma Emission Spectrometry
   03 Axial - Inductively Coupled Plasma Emission Spectrometry
   04 Inductively Coupled Plasma Mass Spectrometry
   05 Cold Vapor Atomic Absorption Spectrometry
   06 Hydride Generation (AAS, ICP/OES, ICP-MS)
   07 DC Plasma Emission
   09 Ion Chromatography - EPA Method
   11 Thermal Ionization Mass Spectrometry
   12 Neutron Activation Analysis
   13 X-ray Fluorescence
   14 Hg per SW846 Method 7473 (AAS)
   15 Kinetic Phosphorescence Analyzer (KPA)
   99 Other

2. The second pair of digits designates the sample preparation method.

   00 No preparation - analyzed as received
   01 SW846 Methods 3005, 3010, 3020, 3050 or CLP ILM03.0
   02 SW846 Methods 3015, 3051 (Microwave assisted)
   05 Total Metals Analysis (i.e. XRF, Fusion, neutron activation)
   06 SW846 Method 3050B, Section 7.5, Increased Solubility
   07 Mercury per SW846 Method 7470 or 7471
   08 Mercury per SW846 Method 7473 (Thermal Decomp/AAS)
   09 Mercury per SW846 Method 7474
   10 EPA Method 200.2 Sample Preparation Methods
   11 EPA Method 200.7 Trace Metals in Waters & Wastes
   12 EPA Method 200.8 Trace Metals in Waters & Wastes
   13 EPA Method 200.9 Trace Elements
   14 SW846 Methods 3052 (Microwave assisted Total Decomposition)
   99 Other

3. The final digit is a letter (A through Z) indicating the sample size (see Appendix D).

APPENDIX D

Sample Size Table

For all analyte types (radiological, and inorganic), the final digit in the Method Code is a letter A through Z and indicates the sample size as shown in the following table:

A less than 1 gram or 1 milliliter

B 1 to 5 grams or 1 to 5 milliliters

C 6 to 10 grams or 6 to 10 milliliters

D 11 to 30 grams or 11 to 30 milliliters

E 31 to 75 grams or 31 to 75 milliliters

F 76 to 100 grams or 76 to 100 milliliters

G 101+ grams or 101+ milliliters

H Small Vegetation

I Large Vegetation

X Entire Sample

Z Air Filter

APPENDIX E

Mixed Analyte Performance Evaluation Program (MAPEP)

Data Entry Instructions

PRELIMINARY CONSIDERATIONS:

The data entry software has been tested primarily with Microsoft's Internet Explorer and Google Chrome. Due to the multiplicity of potential Internet web browsers, products other than Microsoft's Internet Explorer or Google Chrome may operate the reporting software with or without issues. Laboratory personnel using other products should test their browser with the reporting software to ascertain if any issues arise.

For each test session, while MAPEP is awaiting all laboratory data to be entered, the MAPEP system is in read/write mode. **Users may enter, edit and/or delete any current data until the closing date.** After the MAPEP closing date for the test session, the reporting system is placed into read only mode so users can only review the data they have entered into the system or review previous MAPEP studies. When a new test session starts and the MAPEP PT samples are distributed, the MAPEP system will once again be ready for data entry for the new sample.

DATA ENTRY AND/OR EDITING:

1) Start your computer's Web Browser software.

Type in the URL: https://mapep.inl.gov/

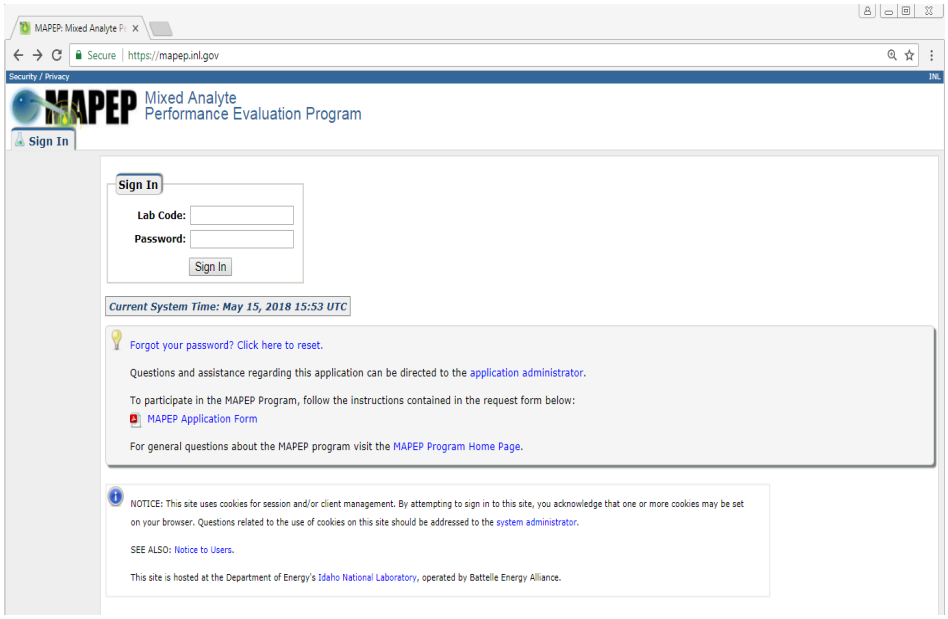
WARNING: You should ***LOG OFF*** the data entry program. Simply closing your browser will not log you off the MAPEP server and additional attempts to LOG IN will fail until the system resets itself (approximately 20 minutes).

The Following Welcome screen appears:

1) Enter your Lab Code and password and then Click on the Login Button.

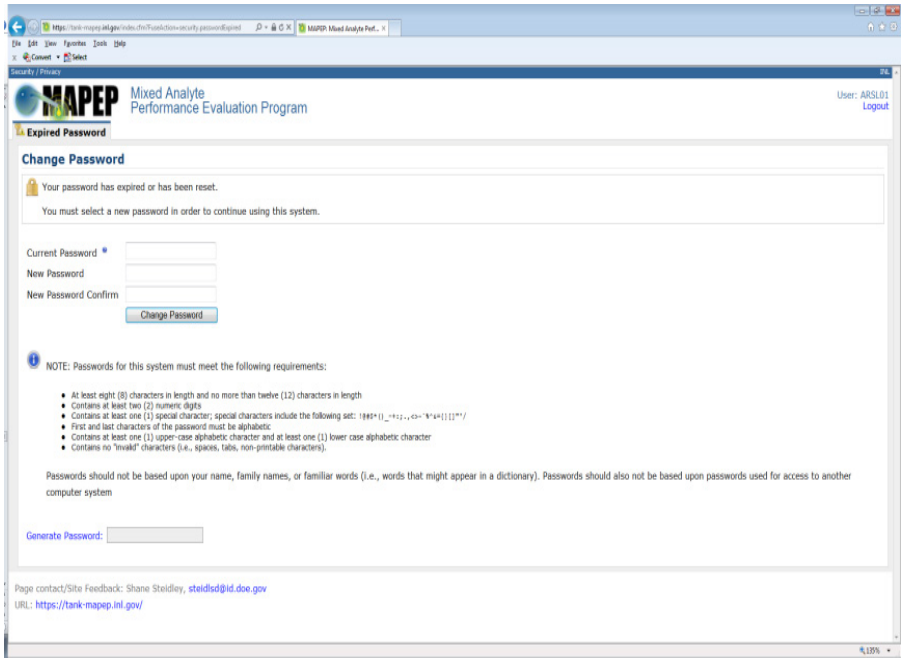
If you forget your password, click on the "Forgot your password?" link to have the password emailed to your MAPE P point of contact.

NOTE: Laboratories passwords must meet certain security criteria (see below).

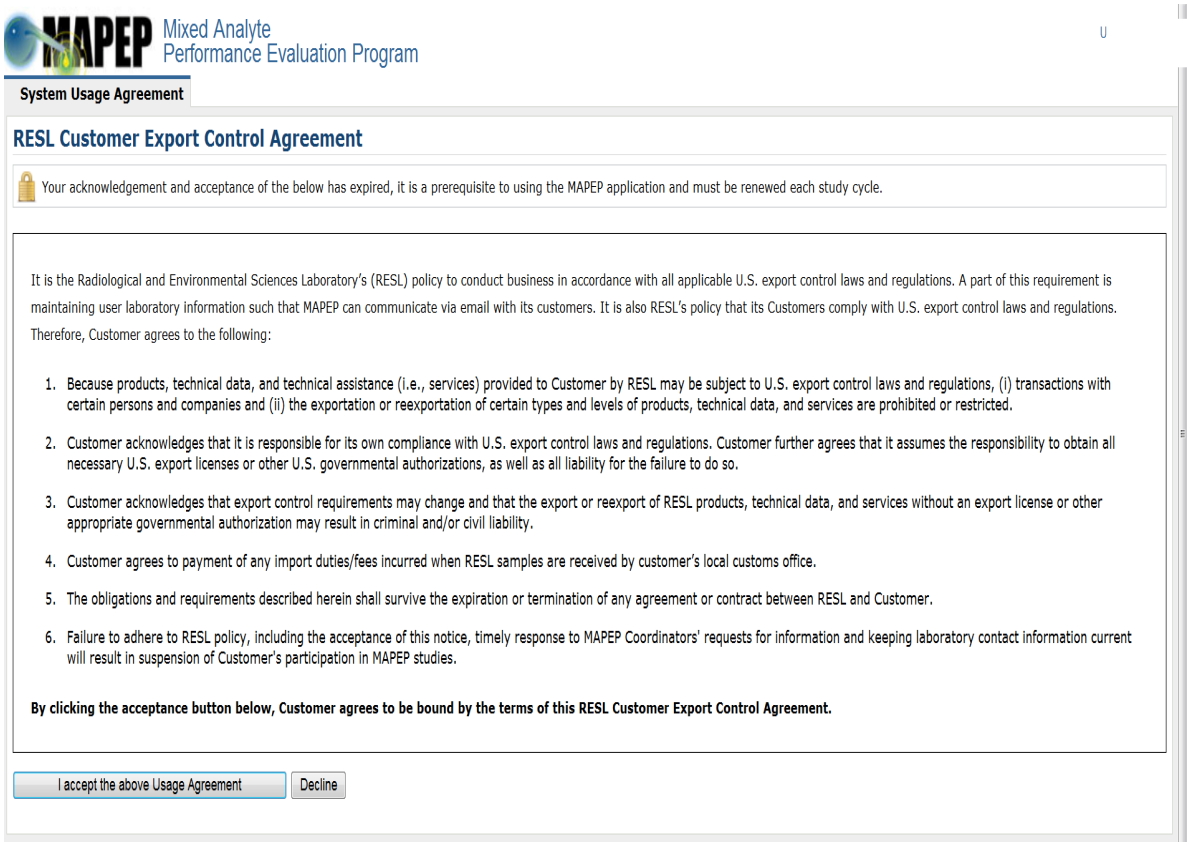


The MAPEP reporting system requires passwords to be changed or updated every six months. The system will automatically prompt the user to select a new password after your password has expired at login. Passwords must meet the criteria outlined on the Change Password screen for security reasons.

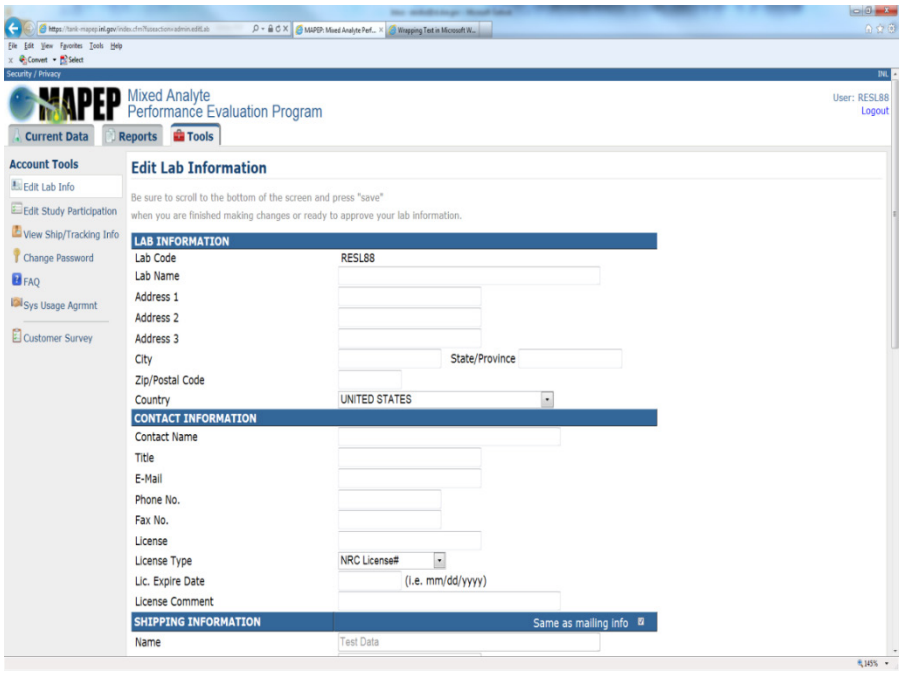
There is a "Generate Password" tool incorporated into this screen that will allow you to generate a compliant password if you desire. Just click on this link and a pop-up window will appear with a suggested password.



2) The RESL Customer Export Control Agreement is displayed and the customer agrees to be bound by the terms of this RESL Customer Export Control Agreement.



3) Users are required to maintain the Laboratory Information up to date, as this is the contact information MAPEP will use for communicating with the participants.



For each new study, the MAPEP users must validate the laboratory information before they can enter data.

To change data in a cell, click in that cell.

DO NOT ENTER POST OFFICE BOX INFORMATION IN THE SHIPPING INFORMATION AREA.

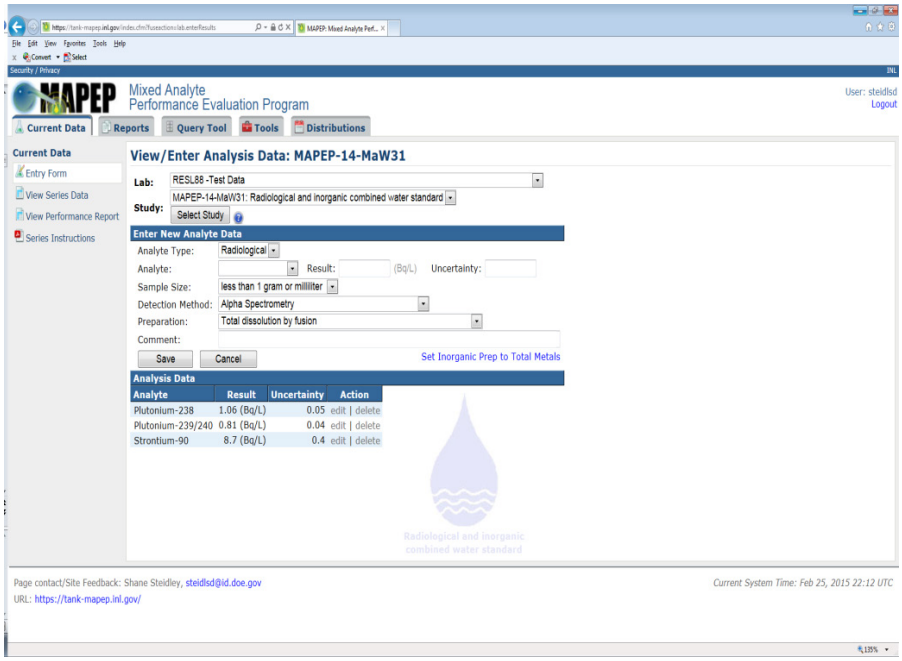
The participant's NRC license or state license number, and the expiration date, must be provided for all United States Laboratories. If a license exemption applies, the user must enter the appropriate DOE contract number and expiration date. A U.S. Federal Laboratory (owned and operated by the federal government, i.e., the laboratory must have federal employees, not an M & O contractor) may enter any appropriate license information or select the federal laboratory option. A foreign laboratory (outside U.S. jurisdiction) will not see the NRC License request, as this option does not apply.

When users get to the shipping information, they may elect to check the "Same as Mailing Info" or "Same as Contact Info" to help provide information for shipping.

Once the user has updated their laboratory information, at the **bottom** of the screen click the **SAVE** button.

Users may now enter their analytical data:

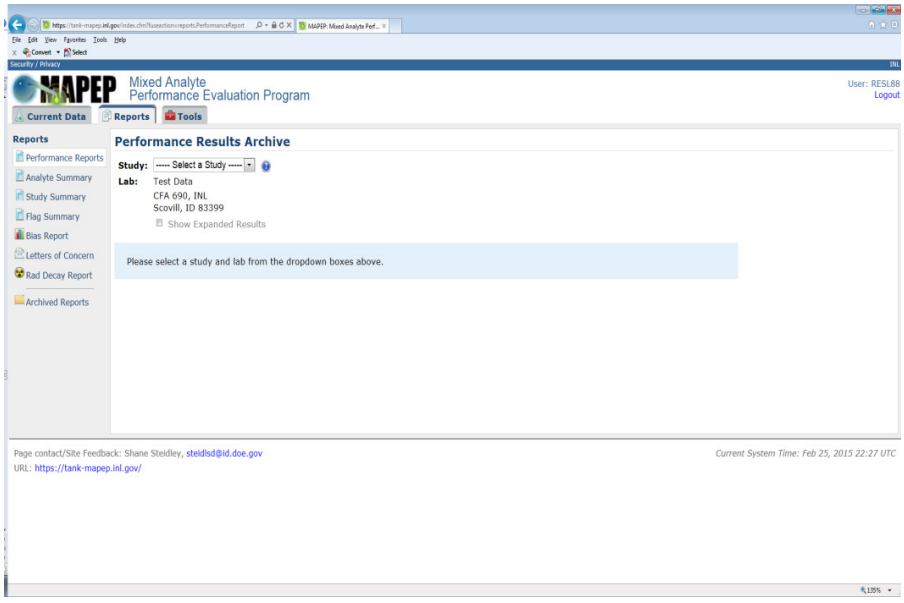
4) As long as the data session is open, you may click on "Entry Form" to input or edit your results.



Select the appropriate analyte type (radiological, inorganic, gross alpha/beta) to start reporting data. The appropriate analyte list, units, and potential method codes are presented based upon the analyte type selected.

After each data point has been entered, the user must click the SAVE button at the bottom of the data entry area to save the data. The list of data entered appears below the data entry area. You will notice that to the far right of each of the analytes entered there is an "edit | delete" action button. This allows users to edit the data entered for the analyte chosen or you may delete that analyte as necessary. When the mouse pointer hovers over the name of the analyte, a small pop-up window appears and provides details of the data you have entered.

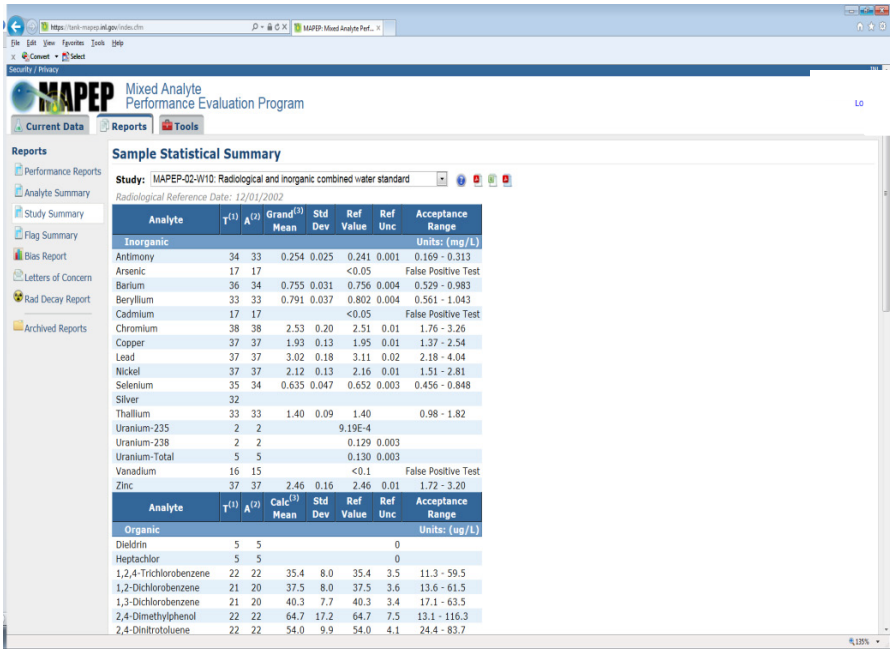
5) From the data entry screen, you may elect to go to the REPORTS section of the Website. The user can view and/or printout their laboratory's PERFORMANCE REPORTS or Certificates of Analytical Performance.



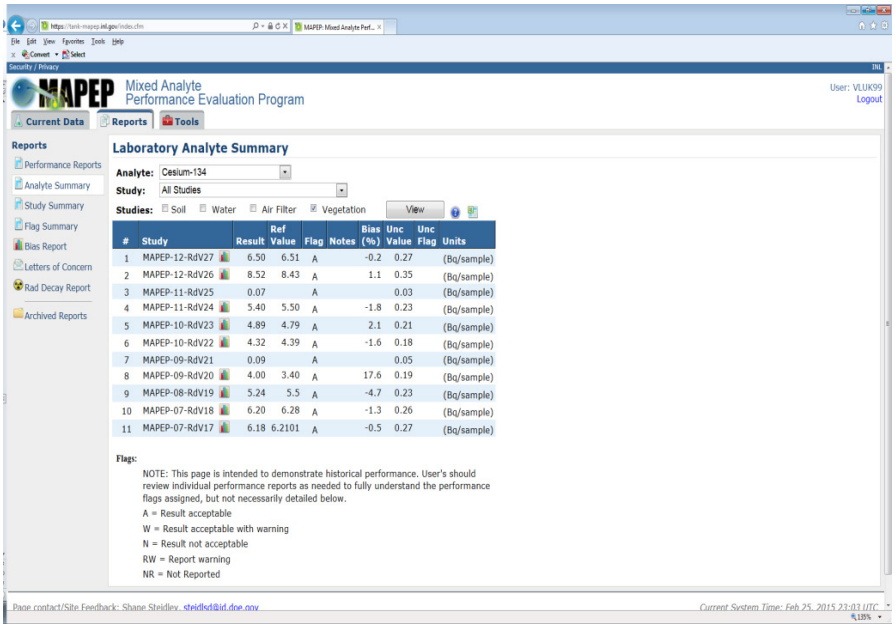
6) Selection of the ANALYTE SUMMARY report allows users to review their historical performance for any analyte they have reported earlier.

Clicking on the Series Identifier rather than a particular matrix will retrieve all results for that Series.

From the dropdown menu window, select an analyte you wish to review. Then select whether you wish to review this performance in soil, water, air filter vegetation, synthetic fecal, or synthetic urine. Finally, click the VIEW button to retrieve the analyte specific performance data.



7) Study and Flag SUMMARY reports allow users to review the historical performance of past studies. Click on this menu item to generate a report like the one to the right.



DATA MODIFICATION OR DELETION

If it is desirable to modify or delete data entries from the data entered, click on the "ENTER RESULTS" menu item while the study is open. The list of analytes entered will appear below the data entry area. To the far right of each of the analytes you will notice the "edit | delete" selection. Selecting the "edit" function will allow you to edit the data entered for this analyte. Selecting the "delete" function will delete the analyte from the list of analytes reported and from the database.

LOG OFF

To exit the MAPEP data entry program, select LOG OFF from upper right menu bar. Your data and information will be saved for your update and/or review at any time.

DO NOT CLOSE YOUR BROWSER PROGRAM (WINDOW) UNTIL YOU HAVE LOGGED OFF. DOING SO MAY LOCK YOU OUT OF ADDITIONAL SESSIONS FOR 20 MINUTES UNTIL THE SERVER RESETS ACCESS.

Keep the password, instructions, and any hard copy in a secure location. If you have problems or questions, please email DOEIDmapep@id.doe.gov. Include your lab code/user id with all communications.

APPENDIX F

Mixed Analyte Performance Evaluation Program (MAPEP)
Proficiency Testing (PT) Material Production and Verification

MAPEP PT standards meet these general characteristics for each MAPEP test session.

Preparation and Production of MAPEP standards:

Whole-volume PT standards for each sample matrix are prepared in sufficient quantities to provide PT material for all the participating laboratories plus homogeneity, verification, and stability testing for the test session. Extra PT standards are archived for additional sample requests. The whole-volume MAPEP PT materials are prepared specifically for traceability to the National Institute of Standards & Technology (NIST).

- MAPEP PT standards use radiological and stable inorganic analytes mixed together in the same soil and water PT sample. This not only ensures a more representative real-world mixed analyte sample, but also provides an efficient means for laboratories to demonstrate their analytical proficiencies.
- MAPEP is performance based and does not dictate the analytical methods, sample size, count time, or other analytical parameters used.
- MAPEP participants use their routine analytical procedures for the analysis of MAPEP PT standards.
- MAPEP PT standards use only whole-volume PT material. Participants will not receive a concentrated volume of PT material that requires subsequent dilution to achieve some specified final volume or concentration. Whole-volume MAPEP standards help prevent special handling or the use of special methods for performance testing. For example, if participants are sent a 5-mL ampoule of concentrated material and are directed to dilute the ampoule to a final 1-L volume, the participant can analyze the concentrated portion as well as the diluted portion and compare results. Whole-volume PT material prevents this possibility and ensures the PT material is treated the same as a real-world sample.
- MAPEP PT standards use real-world natural ground or surface water and soil samples spiked with mixed analytes (radiological and stable inorganic) that are directly traceable to NIST.
- MAPEP PT standards use real-world air filters and vegetation spiked with radionuclides directly traceable to NIST.
- MAPEP does not use single-analyte, purified PT material for any PT sample matrix.
- MAPEP PT standards are homogeneous, reproducible, and stable for the time required to conduct the MAPEP test session (at a minimum). Specific information about homogeneity testing is given below.

- MAPEP PT standards use a representative number of target analytes from those found in Appendix A.
- MAPEP PT standards contain constituents that cause known analytical and preparatory interferences in addition to the target analytes. Participants are therefore tested in the application of any necessary interference corrections.
- MAPEP standards contain gamma-emitters that exhibit random and coincident summing. Participants are tested for random and/or coincident summing corrections in gamma-ray spectrometry.
- MAPEP PT materials are verified with the same gamma-ray detectors and counting geometries used to demonstrate NIST traceability.
- MAPEP mixed analyte soil (MaS) PT standards demonstrate homogeneity with selected radionuclides such that individual 1-g aliquots of soil from each batch of mixed analyte PT material of about 50,000 grams do not vary by more than 5% from the known NIST reference values.
- Radioactivity is homogeneously distributed over the entire area of each MAPEP PT air filter.
- The radioactivity of each individual radionuclide does not vary by more than 1.0% among the MAPEP air filter PT standards. Radioactivity among the vegetation PT standards does not vary by more than 1.0%.
- MAPEP PT material challenges the routine analytical capability of participants in the areas of chemical and radiochemical interferences, measurement accuracy and precision, measurement sensitivity, and false positive/negative results (see below).
- MAPEP PT standards include low-energy beta emitters, including Ni-63 and Fe-55, in both the water and soil matrices. Both of these radionuclides are of interest to DOE for testing low-energy beta analytical methods.
- MAPEP PT standards contain Tc-99 in the water and soil matrices. The Tc-99 is homogeneously distributed in addition to the other radionuclides of interest and remains chemically stable, non-volatile, and has a NIST traceable reference value. Tc-99 is an important radionuclide of interest for DOE and is included in the performance evaluations for these matrices.
- MAPEP PT standards occasionally use refractory plutonium among the various test sessions and PT sample matrices. Analysis of refractory plutonium is an important quality issue for DOE environmental programs and analytical performance.
- MAPEP PT standards periodically use uranium in soil and other matrices difficult to dissolve. Front-end sample dissolution problems frequently lead to inaccurate, unreliable results; acid-insoluble uranium is an important quality issue for DOE environmental programs and analytical performance.
- MAPEP PT standards incorporate antimony in soil and test to ensure participants use analytical methods for increased solubility during sample preparation, such as digestion with

hydrochloric acid and nitric acid. EPA-HQ states in a letter to MAPEP that inorganic methods for the determination of antimony in soil must use increased solubility techniques and that the failure to do so is unacceptable.

- MAPEP PT standards test for specific analytical capabilities that are of importance for DOE analytical services. Participants that fail to meet the MAPEP acceptance criteria are not excused for poor performance, even if most other participants also choose a poor methodology and fail. This is especially true for refractory plutonium, antimony in soil, insoluble uranium, and other problem analytes where poor analytical performance is associated with inappropriate methodology.
- The MAPEP PT standards are verified with radiochemical sample dissolution techniques that guarantee total dissolution of the PT sample. This includes the dissolution of any refractory constituents contained in the sample. Total dissolution techniques are required to ensure accurate verification of the reference values.
- The MAPEP PT standards are verified with radiochemical procedures that use sequential chemical separation procedures for the determination of the actinides. Sequential separation procedures are required to ensure that consistent analytical results are obtained from the same sample aliquot.
- The MAPEP PT standards are verified with radiochemical procedures that use perchloric acid to ensure the complete wet oxidation of organic material. Other analytical methods cannot perform the wet oxidation as completely or as quickly as perchloric acid, and both factors are important to the quality of the verification process.
- Hydrofluoric acid is also used in radiochemical procedures, frequently along with perchloric acid, to assist in the front-end total sample dissolution. Chemical procedures that use hydrofluoric acid to dissolve silicates and oxides generally do so more efficiently, quickly, and completely than those that do not – such factors are important to the quality of the verification process.
- MAPEP PT standards are prepared for false positive/negative testing and sensitivity evaluations in each test session.
- MAPEP PT standards ensure test sessions vary in complexity over time. Each test session is unique with varying PT sample parameters. PT standards vary with the choice of target analytes, specific analyte concentrations, interferences, isotopic ratios, refractory PT material, natural/depleted/enriched uranium, analytes targeted for false positive/negative testing or sensitivity evaluations, choice of matrix material, and other sample parameters.
- MAPEP PT standards rotate the radiological and stable inorganic analytes of interest for accuracy, sensitivity, and false positive/negative testing in the PT sample matrices for each PT test session to ensure complexity and variability among test sessions.
- A radiological or stable inorganic master spiking solution that contains all targeted analytes for a given PT standard matrix shall not be diluted or concentrated and used in a subsequent PT standard matrix.

- The variation in MAPEP PT standard complexity ensures MAPEP test sessions are not duplicated and reference values cannot be derived from previous test sessions, or from a ratio of the reference values used in a previous test session for any of the PT sample matrices.
- MAPEP PT standards use target analyte concentrations typically well above detection limits, but specific analytes are tested at relatively low concentrations from time to time among test sessions to provide variety and complexity in the PT material.
- MAPEP PT standards for gross alpha/beta measurements in water and air filter matrices use Th-230 and Sr-90 or other equivalent radionuclides that ensure only alpha and beta measurements are performed. For example, Am-241 and Cs-137 are not used for gross alpha/beta PT standards because they emit gamma rays which can be used by gamma-ray spectrometry to make the measurement.

Measurement Traceability of PT Standards:

MAPEP reference values for the target analytes in the PT standards are directly traceable to NIST. Uncertainties shall be calculated for all reference values according to the ISO/IEC/OIML/BIPM *Guide to the Expression of Uncertainty in Measurement (GUM:1995*); NIST Technical Note 1297, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results (1994)*; or other authoritative standard references.

- MAPEP PT standards use scientifically valid and legally defensible reference values with associated uncertainties and documented verification data in accordance with ISO/IEC 17043 (see below).
- MAPEP PT standard results are evaluated to a scientifically defensible acceptance criteria.
- The reference value for radiological and stable inorganic analytes is calculated from the NIST certified standard value and the standard dilution(s) used. The reference value shall not be determined by the experimental analysis of the sample. Rarely, a radiological or stable inorganic reference value is derived from sample characterizations.
- Total uncertainties for the reference values shall not be determined empirically but rather by mathematical error propagation of the uncertainty of the NIST certified standard value and the uncertainty associated with the standard dilution(s) used in constructing the sample. Therefore, the total uncertainty for the radiological and stable inorganic reference values is minimized because they are based on mathematical calculation and not experimental error.
- A Radiological Traceability Program (RTP) with NIST involves a two-way exchange of material between RESL and NIST used to demonstrate direct traceability of the analytical methods used by RESL for MAPEP PT material preparation and verification. RESL prepares material for analysis by NIST and RESL blindly analyzes material prepared by NIST. All MAPEP PT matrices and radiological analytes are used in this two-way exchange. RESL is the only laboratory that utilizes a NIST RTP program.

MAPEP utilizes the individual analytes listed in Appendix A of the MAPEP Handbook. There are 8 major analyte/matrix categories:

1. Mixed Analyte Soil (MaS) matrix. MAPEP uses a natural soil characterized for background activities of target radionuclides and background concentrations of target inorganic compounds.
2. Mixed Analyte Water (MaW) matrix. MAPEP uses naturally occurring water (well, sub-surface, surface, spring, river, lake, etc.) characterized for background activities of target radionuclides and background concentrations of target inorganic analytes. The MaW water is not prepared from deionized or distilled water.
3. Radiological analytes in a vegetation (RdV) matrix. MAPEP uses a naturally occurring grass-type vegetation matrix characterized for background radionuclide activities.
4. Radiological analytes in an air filter (RdF) matrix. MAPEP uses 47-mm glass fiber filters characterized for background radionuclide activities.
5. Gross alpha/beta radionuclides in water (GrW) matrix. MAPEP uses naturally occurring water characterized for background radionuclide activities.
6. Gross alpha/beta radionuclides in air filter (GrF) matrix. MAPEP uses 47-mm glass fiber filters characterized for background radionuclide activities.
7. Special Radiological Matrix (XrM). MAPEP prepares specially selected radionuclides in a difficult sample matrix. The participants receive little information pertaining to the sample matrix and the targeted radionuclides so that the sample is largely unknown. Each reported XrM result will have the bias from the RESL known value calculated, but the reported results will not be flagged or evaluated by any acceptance criteria. The goal is to allow participants to test their capabilities on a variety of unknown sample matrices and analytes without the fear and potential ramifications that may result from a poor performance evaluation.
8. Mixed Analyte Synthetic Fecal (MaSF). MAPEP utilizes ingredients found within real fecal matter to mimic a real-world radiobioassay sample. The PT samples are prepared in individual containers for sequential spiking with NIST-traceable standards. They are refrigerated until distributed.
9. Mixed Analyte Synthetic Urine (MaSU). MAPEP utilizes ingredients found within real urine to mimic a real-world radiobioassay sample. The PT samples are prepared in individual containers for sequential spiking with NIST-traceable standards. They are refrigerated until distribution.

Specific Activities and Concentrations for Analytes Listed in Appendix A

The target analyte specific activity or concentration is typically well above detection limits, but the amount of PT material provided for each participant is limited. Therefore, the specific activity and concentration ranges indicated in the sample description should be used to select the optimum quantity of sample for each analysis.

Guidelines for Radiological Specific Activities:

- Specific activities for target radionuclides are representative of levels expected in the DOE Complex, for DOE-site characterization, remediation, environmental monitoring, and long-term stewardship. Specific activities span the range of the radiological methods and instrumentation used in these environmental programs.
- Specific activities do not exceed Department of Transportation (DOT) shipping regulations for non-radioactive shipments.
- Specific activities are sufficient for most radionuclides to provide less than 5-10% counting uncertainty with a reasonable sample size and count time.

Guidelines for Inorganic Analyte Concentrations:

- Stable inorganic analyte concentrations typically do not exceed the Resource Conservation and Recovery Act (RCRA) limits for hazardous material.
- Lower concentration limits for stable inorganic analytes are based on the EPA's Contract Laboratory Program (CLP) Quantitation Limits (ILM05.3 SOW), however, this does not limit the use of false positive/negative testing and sensitivity evaluations for the inorganic analytes.
- Stable inorganic analyte concentrations are dependent on the target analytes of interest and the instrument/method of analysis. For example, refer to the target analyte quantitation levels as described in the EPA's CLP ILM05.3 SOW.
- Analyte concentrations shall be sufficient to allow measurement uncertainties of 5-10% for most stable inorganic analytes.

False Positive/Negative Testing and Sensitivity Evaluations

False positive/negative testing and sensitivity evaluations are used in radiological and stable inorganic performance evaluations. The specific analytes used for testing vary among PT test sessions.

Radiological/Inorganic Analytes

The radiological false positive/negative and sensitivity evaluation tests are based in part on information found in ANSI N42.23 and several measurement uncertainty papers by Lloyd A. Currie.

1) The MAPEP program uses false positive testing to identify laboratory results that indicate the presence of a particular radionuclide or an inorganic analyte in a MAPEP standard when, in fact, the actual activity of the radionuclide or the concentration of the inorganic analyte is far below the detection limit of the measurement. "Not Acceptable" (N) performance, and hence a false positive result, is indicated when the range encompassing the result, plus or minus the total uncertainty at three standard deviations, does not include zero (e.g., 2.5 +/- 0.2; range of 1.9 to 3.1). Statistically, the probability a result can exceed the absolute value of its total uncertainty at three standard deviations by chance alone is less than 1%. MAPEP uses a three standard deviation criterion for the false positive test to ensure confidence about

issuing a false positive performance evaluation. A result greater than three times the total uncertainty of the measurement represents a statistically positive detection with over 99% confidence.

2) Sensitivity evaluations are routinely performed to complement the false positive tests. In a sensitivity evaluation, the analyte is present at or near the detection limit, and the difference between the reported result and the MAPEP reference value is compared to the propagated combined total uncertainties. The results are evaluated at three standard deviations. If the observed difference is greater than three times the combined total uncertainty, the sensitivity evaluation is "Not Acceptable". The probability such a difference can occur by chance alone is less than 1%. If the participant did not report a statistically positive result, a "Not-Detected" is noted in the text field of the MAPEP performance report. A non-detect is potentially a false negative result, dependent upon the laboratory's detection limit for the radionuclide.

3) False negative tests are also performed in combination with the sensitivity evaluations. In this scenario, the sensitivity of the reported measurement indicates the known specific activity of the targeted analyte in the PT sample should have been detected, but was not, and a "Not Acceptable" performance evaluation is issued. The combined uncertainty of the MAPEP reference value and of the reported result at three standard deviations is used for the false negative test.

4) The false positive/negative and sensitivity evaluation tests are conducted in a manner that assists the participants with their measurement uncertainty estimates and helps ensure they are not underestimating or over-inflating their total uncertainties. If the total uncertainty is over inflated to pass a false positive test, it will result in a "Not Detected" and a potential "False Negative" if the test is a sensitivity evaluation. Underestimating the uncertainty for a perceived sensitivity evaluation will yield a potential "False Positive" if a false positive test is performed. Underestimating the total uncertainty can also result in a failed sensitivity evaluation if it can be demonstrated that the sensitivity of the measurement should have detected the specific activity present in the sample, as when uncertainties are very small. An accurate estimate of measurement uncertainty is required for consistent performance at the acceptable level.

PT Standard Verification

MAPEP shall verify the reference values for the MAPEP PT standards of each test session (Series) according to the requirements of ISO/IEC 17043 and the additional following requirements:

- Radiological Reference Value Verification:

  Target radionuclides shall be verified by alpha, beta, or gamma analyses. Radiochemical sample dissolution techniques shall guarantee total dissolution of the sample and dissolution of any refractory compounds contained in the sample. Sample dissolution techniques that use acid leaching as the primary method of dissolution shall not be used. Sequential chemical separation procedures shall be used for the determination of the actinides to ensure consistent analytical results are obtained from the same sample aliquot. Perchloric acid shall

be used safely and on a routine basis to ensure the complete wet oxidation of organic material. Hydrofluoric acid shall be used safely and on a routine basis to assist total sample dissolution and for the dissolution of silicates and oxides. The analytical results from the chemistry procedure shall verify the NIST traceable reference value if the analytical result ± the associated total uncertainty includes the reference value at a 95% (two standard deviations) confidence level. Reference values that include the background concentration of analytes shall also include the uncertainty of the measurement process.

- Inorganic Reference Value Verification:

  Target analytes shall be verified by standard inorganic analytical methods. Reference values that include the background concentration of analytes shall also include the total uncertainty of the measurement process. The analytical results from the chemistry procedure shall verify the NIST traceable reference value if the analytical result ± the associated total uncertainty includes the reference value at a 95% confidence level, or the analytical result is within 10% of the calculated NIST traceable reference value.

Homogeneity Testing for the MAPEP Mixed-Analyte Water and Mixed-Analyte Soil Standards

MAPEP standards shall be homogeneous so that the variability among PT standards shall not contribute significantly to the variability of the results among participant laboratories. MAPEP shall verify the homogeneity of PT material with statistical evaluations of randomly selected PT standards taken from across the range of standards prepared in the PT material production batch. The statistical evaluations shall demonstrate that variability within, and among PT standards, is within acceptable levels. The alpha probability level will be set at 0.05. This means the probability of Type I error, or rejecting a true null hypothesis (i.e., concluding sample heterogeneity when the observed variability is due to chance alone) will not exceed 5%. Statistical confidence limits shall be set at the 95% level. Radiological results shall be within the statistics of the measurement at two standard deviations. In addition, the specific activity of selected radionuclides shall demonstrate that individual 1-gram aliquots of soil from each batch of mixed analyte PT material do not vary by more than 5% from the known NIST reference values. The statistical methods used for homogeneity testing shall comply with the requirements of ISO 17034, ISO/IEC 17043, and ISO 13528. For example, see "The International Harmonized Protocol For The Proficiency Testing Of Analytical Chemistry Laboratories", *Pure Appl. Chem.*, Vol. 78, No. 1, pp. 145–196, 2006.

Indicator analytes, if used, must be carefully selected. Actinides are typically among the most difficult analytes to distribute homogeneously in a soil, and therefore shall be among the indicator analytes of choice. If the indicator analytes or a majority of the homogeneity data demonstrates excessive variation in the PT material, a second set of PT standards shall be analyzed. If homogeneity is still questionable, the sample shall be re-blended and the homogeneity testing repeated. If necessary, the PT material shall be discarded and a new PT batch created.

Homogeneity Testing for the MAPEP Radiological Vegetation and Air Filter Standards

MAPEP air filters and vegetation PT standards are prepared by individually spiking each PT standard with the target analytes of interest. MAPEP air filter and vegetation PT material is not

prepared with a batch methodology. Furthermore, participants are instructed to analyze the entire PT standard; the PT standard cannot be subdivided. Since the PT standards are individually prepared and the entire PT standard is analyzed, variability within the PT standard is not a factor that can influence a participant's results. Therefore, homogeneity testing for within sample variability is not required for the air filter and vegetation PT material. In addition, since the PT standards are individually spiked and not prepared in a batch, any variability among standards cannot be a function of heterogeneity within a batch material or heterogeneity from dispensing the PT material itself. Therefore, homogeneity testing among standards is not required, at least not from a batch standpoint. Variability among standards can only be a factor if the master spiking solution is not homogeneous, or if the spiking quantity is not reliably reproduced. MAPEP shall ensure that the activity on each air filter sample is homogeneously distributed over the entire area of the filter. The MAPEP verification analyses shall also demonstrate the homogeneity of the master spiking solution and the reproducibility of the PT standard spikes. The verification/homogeneity testing shall demonstrate that aliquots from the master spiking solution used for the PT material are statistically identical at the 95% (two standard deviations) confidence level. Furthermore, the variability of the spikes among vegetation and air filter standards shall not exceed 1%.

Stability testing for radiological and stable inorganic analytes:

Radiological and stable inorganic PT standards shall have stability testing performed according to the criteria in ISO 17034 and ISO/IEC 17043. The results of the stability test shall verify the reference value within the statistics of the measurement at the 95% (two standard deviations) confidence level.