



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

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## RESL CUSTOMER EXPORT CONTROL AGREEMENT

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.

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

## 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, stable inorganic, or organic analyses. The proficiency testing (PT) standards used to test analytical proficiencies, however, frequently do not resemble the real-world 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 interference. The environmental samples submitted for analysis, however, typically have multiple target analytes in a whole-volume, non-concentrated and non-purified, natural matrix sample with numerous chemical or other interferences. Additionally, since the PT material is prepared for either radiological, stable inorganic, or organic analyses, the combined analytes are not in the same PT standard. Yet, the environmental samples that DOE must analyze typically contain constituents from each analytical category mixed together. Regulatory requirements frequently include analyses of radiological and non-radiological "mixed analytes" from the same environmental sample. 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), under the program direction of the DOE-HQ, shall administer the MAPEP. MAPEP standards, distributed twice a year, include mixed analyte water and soil matrices with environmentally important radiological, stable inorganic, and organic constituents included in the same PT standard. 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 PTP 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.

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## II. PARTICIPATION

All laboratories that perform environmental analytical measurements for DOE (i.e., radiological, stable inorganic, and/or organic analyses, 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).” MAPEP participation for radiological laboratories is also required by the DoD/DOE Quality Systems Manual for Environmental Laboratories (QSM, current version). It is important to note that MAPEP PT standards are a mixed-analyte Certified 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 and as described in the DoD/DOE QSM (current version), and implementing any corrective actions necessary.

MAPEP participation may be requested by emailing a request to [MAPEP@id.doe.gov](mailto:MAPEP@id.doe.gov). MAPEP applications are also available under the program information link on the MAPEP public website at <http://www.id.energy.gov/resl/mapep/mapep.html> or <https://mapep.inl.gov/>. A request for participation should include a shipping and correspondence address, a contact person for each, appropriate phone numbers, FAX number, 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 and a QA/QC plan. Guidance for the QA/QC plan can be found in the DoD/DOE QSM (current version). 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.

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### III. SAMPLE PREPARATION, CHARACTERIZATION, 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 2-5% (v/v) nitric acid and characterized natural ground or surface water. Organic analytes in water and soil are added to a separate whole-volume sample. The organic water and soil standards do not contain spiked radiological or stable inorganic components. All sample containers are acid-washed polyethylene or pre-cleaned 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 in accordance with ISO Guide 43. Known values for organic analytes are derived from vendor certified standards and procedures that are in accordance with ISO 17043 (see Appendix G). Sample handling and storage procedures are similar to those for the liquid PT standard. Appendix G delineates the requirements for MAPEP PT standards material preparation and verification in accordance with Proficiency Testing Provider requirements operating under a Quality System that complies with, and is accredited to ISO 17025, ISO 17043 and ISO Guide 34.

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.

### IV. SAMPLE DISTRIBUTION

Standards are distributed semi-annually. Sample descriptions and instructions will be available on the Internet prior to each sample distribution. Current Sample Descriptions can be found on the public MAPEP website at <http://www.id.energy.gov/resl/mapep/mapep.html> for all MAPEP proficiency testing matrices. The MAPEP must be notified of any special shipping requirements. The participants must ensure that 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 that 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.

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## V. 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/organic 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.

## VI. REPORTING RESULTS

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

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

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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. The MAPEP strongly encourages that all results, including organic analyses, be reported with uncertainty estimates. If the reported result is actually 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 N42.14-1999; 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:

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

where  $\mu$  = the combined uncertainty and the other variables are as described above.

For example, let R = the analytical result,  $\Delta R$  = the total combined uncertainty in the result. Let U1 = an uncertainty component involved in the calculation of the result (such as a pipette calibration),  $\Delta U1$  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,  $\Delta U2$  = 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,  $\Delta U3$  the uncertainty in the weight measurement; let U4 = a fourth uncertainty component, such as a volume measurement,  $\Delta U4$  = the uncertainty in the volume measurement, etc. Note that all uncertainty components, including Type B uncertainty, should be estimated at one

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standard deviation. The equation used to calculate the total combined uncertainty in the result is given by:

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

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.

When entering organic analytical results, the uncertainty field associated with the result is optional for input. If the laboratory propagates uncertainties for the analytes being reported, then the uncertainty field must be used to record the uncertainty result for the organic analyte. 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, NIST, and other references cited above. Understanding the uncertainty of measurements is crucial for quality control and the improvement of radiological, stable inorganic, and organic analytical methods.

The MAPEP does not require a laboratory to calibrate for more organic components than they typically perform for other DOE work. Laboratories may utilize “less than” values for organic target analytes to signify a calibrated component when the results are below the detection limit. 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.

## VII. 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 and acceptance criteria for targeted analytes are:

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

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$$\% \text{ BIAS} = \frac{(100)(\text{LABORATORY RESULT} - \text{RESL REFERENCE VALUE})}{\text{RESL REFERENCE VALUE}}$$

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

- 1) ACCEPTABLE ..... BIAS <= 20%
- 2) ACCEPTABLE WITH WARNING.... 20% < BIAS <= 30%
- 3) NOT ACCEPTABLE ..... BIAS > 30%

**For each reported organic analyte**, the laboratory result is graded in accordance with NELAC Institute Performance Criteria as specified in the appropriate Field of Proficiency Testing (FoPT) tables associated with each matrix. The semi-volatile organics water standard is evaluated using the spiked value as the true value “T” (assigned value). The acceptance limits for this standard are generated utilizing the linear regression line found in the July 2007 Non-potable water FoPT tables. The MAPEP does not require a laboratory to calibrate for more organic components than they typically perform for other DOE work. See the above discussion regarding the use of “less than” values and when not to report results. A laboratory’s failure to detect a spiked component (i.e., a “less than” value is reported, but the component’s concentration is above that limit) is a false negative and is flagged as “Not Acceptable” (N).

**For the organics in water PT standard**, a Z-Score is generated using the calculated mean and calculated standard deviation derived from the FoPT:

$$Z\text{-Score} = \frac{(\text{LABORATORY RESULT} - \text{Calculated MEAN})}{\text{Calculated STANDARD DEVIATION}}$$

**The soil reference values for the organic target analytes** are determined as the biweight mean<sup>1, 2</sup> of all laboratory data for the analyte. The acceptance limits for this standard are generated utilizing the linear regression line found in the solids/soil NELAC FoPT tables. Where the population mean is required for determining a reference value, the calculation used is analogous to the classical confidence interval for the mean of a population:

$$T_{bi} \pm (t_{(0.95, n-1)}) * \frac{S_{bi}}{\sqrt{n}}$$

Where  $T_{bi}$  = Biweight mean  
 $S_{bi}$  = Biweight standard deviation  
 n = Number of observations

1 Kafadar, K. (1982), “A Biweight Approach to the One-Sample Problem”, *Journal of the American Statistical Association*, 77, 416-424.

2 ISO Guide 43, *Proficiency Testing by Interlaboratory Comparisons*, Second Edition, 1997

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$t_{(0.95, n-1)}$  = Student's t value at the 95% confidence interval and n-1 degrees of freedom.

**For the organics in soil PT sample**, the mean of all reported results and the standard deviation of all results (less outliers) are used to calculate a Z-Score:

$$Z\text{-Score} = \frac{(\text{LABORATORY RESULT} - \text{MEAN OF ALL DATA})}{\text{Standard Deviation of all data OR Calculated Standard Deviation from FOT tables.}}$$

The Z-Score for the semi-volatile organics places the laboratory result in one of two categories:

- 1) ACCEPTABLE (A) .....  $0.0 < Z\text{-Score} \leq 3.0$
- 2) NOT ACCEPTABLE (N) ....  $Z\text{-Score} > 3.0$

**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 for an analyte is not currently used as part of the acceptance criteria, but it will be used to flag a potential area 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.

MAPEP will assign radiological and stable inorganic uncertainty flags A, W, N. Relative precision is defined as the ratio of the precision of a given measurement and the value of the measurement itself. The uncertainty flag criteria are:

- 1) NOT ACCEPTABLE .....  $RP < 2\%$
- 2) ACCEPTABLE .....  $2\% \leq RP \leq 15\%$
- 3) ACCEPTABLE WITH WARNING...  $15\% < RP \leq 30\%$
- 4) NOT ACCEPTABLE .....  $RP > 30\%$

Reported total uncertainties are used to evaluate performance in false positive/negative tests and sensitivity evaluations (see Appendix G). 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. False positive/negative tests are performed for organic results, however, performance assessment differs from radiological and inorganic methodology.

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## VIII. 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. 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. MAPEP routinely issues Letters of Concern to point out 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.

MAPEP data will also be forwarded to the DOE-HQ Analytical Services Program Manager and other DOE-HQ contacts, DOE Field Offices, Sample Management Offices, the DOE Consolidated Audit Program (DOECAP), and other MAPEP stakeholders. DOECAP will review the overall performance of the laboratory in concert with other performance evaluation programs and identify any additional concerns.

## IX. 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, and final PT reports. Performance evaluation reports and program information are provided on the secure MAPEP website and later on the public website at <http://www.id.energy.gov/resl/mapep/mapep.html>. MAPEP participants and stakeholders may also use the MAPEP password protected website at <https://mapep.inl.gov/> where several database tools are available to track and trend historical performance, auditors can prepare for DOECAP audits, and participants receive the MAPEP Letters of Concern regarding potential quality issues.

## X. CRITERIA FOR LETTERS OF CONCERN

The following provides a brief overview of the policies and processes associated with issuing and responding to a Mixed Analyte Performance Evaluation Program (MAPEP) Letter of Concern, and its significance to the Department of Energy's Consolidated Audit Program (DOECAP).

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

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sent to DOE/contractor oversight Points of Contact (POCs), including DOE Field Office and Headquarters POCs, and contractor Sample Management POCs. 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, when any laboratory may question or appeal performance evaluation results. All laboratories have the opportunity to respond to a Letter of Concern by contacting the MAPEP, and many frequently do so. In addition, laboratories can request additional MAPEP standards at any time for verification of measurement processes, and many have utilized this option.

Letters of Concern specifically address an area of significance to the DOECAP, as laboratory participation in proficiency testing (PT) programs is typically assessed during a DOECAP audit. The DoD/DOE QSM (current version) identifies the corrective action and documentation required for a laboratory to address proficiency testing program failure. Corrective action documentation must be available for review during DOECAP audits, and the same documentation should be available for any clients or other stakeholders. If the DOECAP issues a finding in the area of PT performance, including any finding derived from or associated with a MAPEP Letter of Concern, the laboratory has the opportunity to respond and perform corrective actions through the DOECAP process.

In addition to issuing Letters of Concern, the MAPEP Team provides technical assistance whenever requested, to both MAPEP participants and DOE/contractor oversight personnel. That assistance has helped resolve many quality issues, thereby improving the quality of analytical services and

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ultimately reducing potential DOE liability. MAPEP Letters of Concern are instrumental in this process by providing a method of communication that focuses attention on analytical performance, and when used as intended, assists laboratories and DOE/contractor oversight personnel avoid potential quality problems and/or correct quality issues in a timely manner.

It is also important to note that the DOE field site management/personnel, and/or its DOE contractor, that enter into a contractual agreement with an analytical laboratory for field data services, have an important responsibility. They are responsible for assuring that the corrective actions needed to remedy the data discrepancy, as identified by the proficiency testing of MAPEP, satisfy the Department's obligations and provide confidence in the quality, validity, and reliability of the analytical data.

## 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	Lead-212
Lead-214	Manganese-54	Neptunium-237
Nickel-63	Plutonium-238	Plutonium-239/240
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 (continued)

### 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 A (continued)**

### **List of MAPEP Target Analytes**

The MAPEP organic analytes can be found in the  
NELAC PT Fields of Proficiency Testing FoPT for “Non-potable water” and  
“Solid and Chemical Materials”

## Appendix B

### Method Codes for Radionuclides

#### 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
06	PEARLES
07	Kinetic Phosphorescence Analyzer (KPA)
08	Inductively Coupled Plasma Mass Spectrometry
99	Other

#### \*

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

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
12	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
99	Other

#### \*

3. The \* is a letter (A through G) indicating sample size (see Appendix E).

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## Appendix C

### Method Codes for Inorganic Metals

#### INORGANIC METALS

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

00	Flame Atomic Absorption Spectrometry
01	Furnace Atomic Absorption Spectrometry (Zeeman Background Correction)
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
08	Furnace Atomic Absorption Spectrometry (Deuterium Continuum Background)
09	Ion Chromatography - EPA Method
10	Flame Emission Spectrophotometry
12	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 technique.

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
12	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
99	Other

3. The \* is a letter (A through G) indicating sample size (see Appendix E).

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## Appendix D

### Method Codes for Organic Analytes

#### ORGANIC ANALYTES

1. The first pair of digits designates the method of analysis.

00	USEPA Method 601 - Purgable Halocarbons
01	USEPA Method 602 - Purgable Aromatics
02	USEPA Method 608 - Organochlorine Pesticides and PCB's
03	USEPA Method 624 - Purgables
04	USEPA Method 625 - Base/Neutrals and Acids
05	SW-846 8021 Aromatic and Halogenated Volatiles by GC using PID and/or EC
06	SW-846 8041 Phenols by Gas Chromatography
07	SW-846 8061 Phthalate Esters by GC/ECD
08	SW-846 8081 Organochlorine Pesticides by Gas Chromatography
09	SW-846 8082 Polychlorinated Biphenyls by Gas Chromatography
10	SW-846 8091 Nitroaromatics and Cyclic Ketones by Gas Chromatography
12	SW-846 8100 Polynuclear Aromatic Hydrocarbons
12	SW-846 8121 Chlorinated Hydrocarbons by Gas Chromatography: Capillary
13	SW-846 8260 Volatile Organics Compounds by GC/MS
14	SW-846 8270 Semivolatile Organic Compounds by GC/MS
15	SW-846 8275 Semivolatile Organic Compounds (PAHs and PCBs) TE/GC/MS
16	SW-846 8310 Polynuclear Aromatic Hydrocarbons
17	SW-846 GC/GTIR for Semivolatile Organics: Capillary Column
99	Other

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

00	No Preparation - analyzed as received
01	Separatory Funnel Liquid-Liquid Extraction (Method 3510C)
02	Continuous Liquid-Liquid Extraction (Method 3520C)
03	Soxhlet Extraction (Method 3540C)
04	Automated Soxhlet Extraction (Method 3541)
05	Supercritical Fluid Extraction (Method 3560)
06	Ultrasonic Extraction (Method 3550B)
07	Supercritical Fluid Extraction of PAHs (Method 3561)
08	Waste Dilution for Volatile Organics (Method 3585)
09	Purge-and-Trap for Aqueous Samples (Method 5030B)
10	Closed-System-Purge-and-Trap and Extraction for Volatiles (Method 5035)
12	Pressurized Fluid Extraction (Method 3545A)
99	Other

3. The \* is a letter (A through G) indicating sample size (see Appendix E).

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## Appendix E

### Sample Size Table

For all analyte types, the ‘\*’ in the Method Code corresponds to values 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 Air Filter
- I Small Vegetation
- J Large Vegetation

## Appendix F

### 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 Netscape. Due to the multiplicity of potential Internet web browsers, products other than Microsoft's Internet Explorer or Netscape 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.

While MAPEP is awaiting all laboratory data to be entered, the MAPEP system is read/write. **Users may enter, edit and/or delete any current data until the closing date.** After the MAPEP closing date, the reporting system becomes read only so users can only review the data they have entered into the system or review previous MAPEP studies. When a new MAPEP standard is 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).

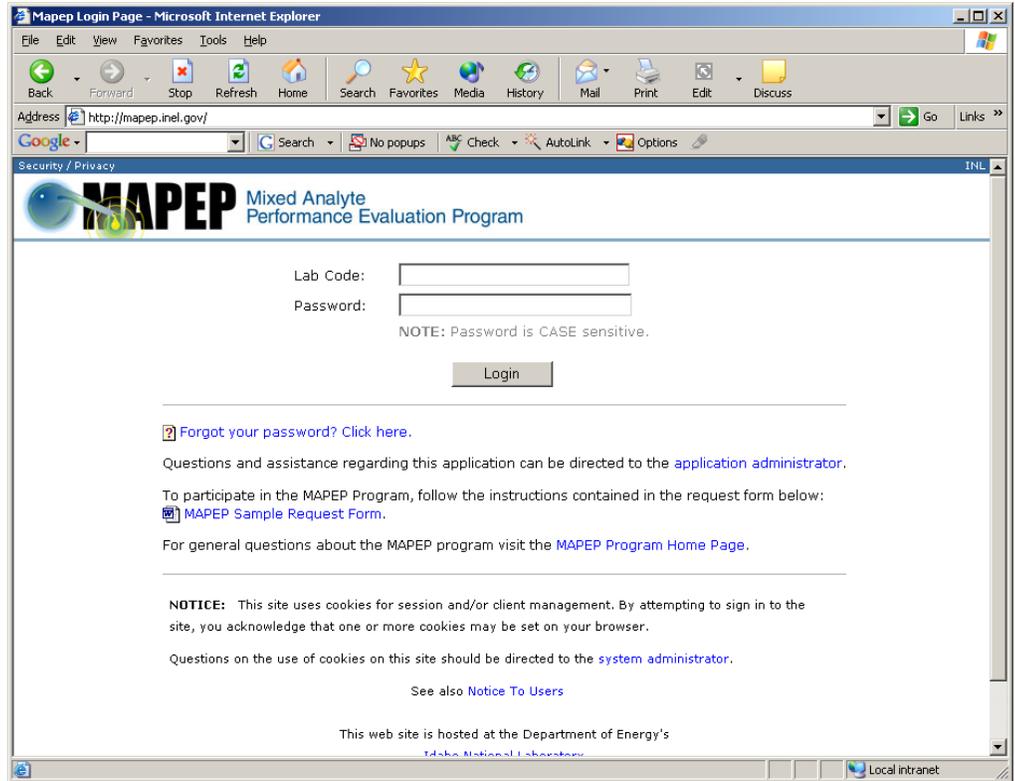
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The Following Welcome screen appears:

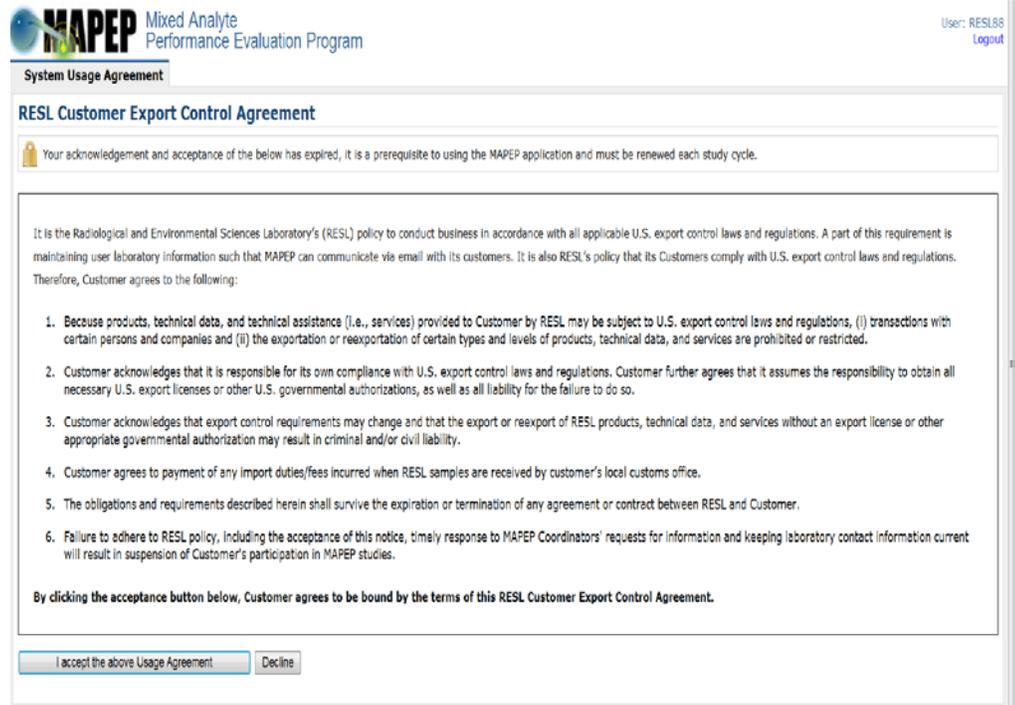
1) Enter your Lab Code and password and then Click on the Login Button.

If you forget your password, click on that link to have the password emailed to your MAPEP point of contact.

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



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.

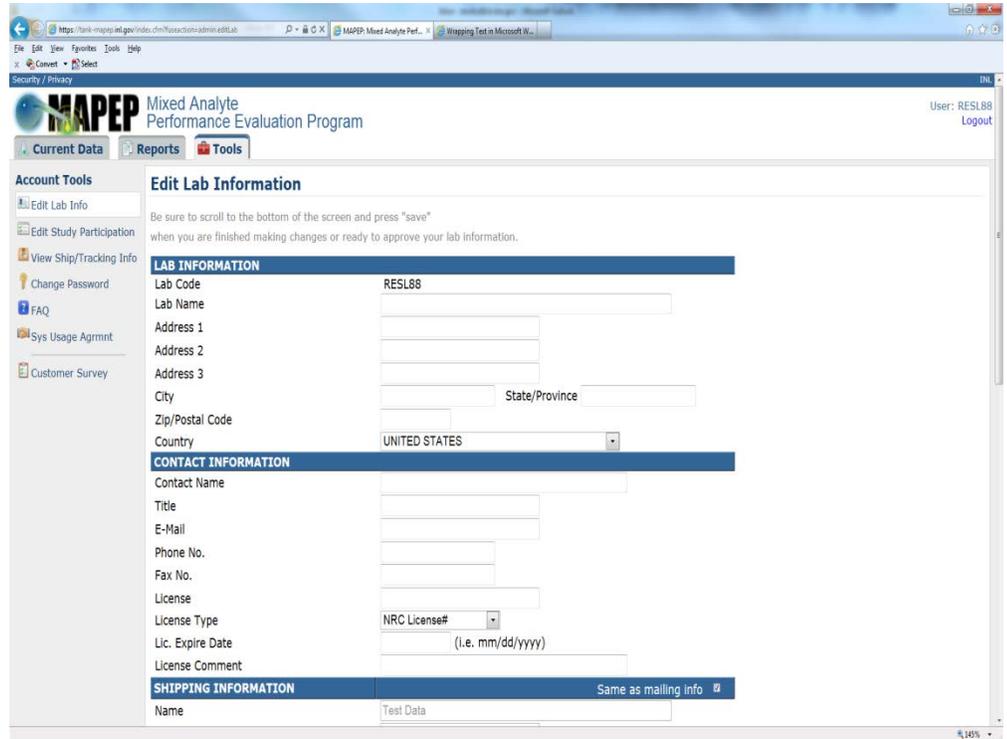


3) Users are required to maintain the Laboratory Information up to date, as this is the contact information MAPEP will use for communicating with the participants.

For each new study, the MAPEP users must validate the laboratory information before they are allowed to 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.

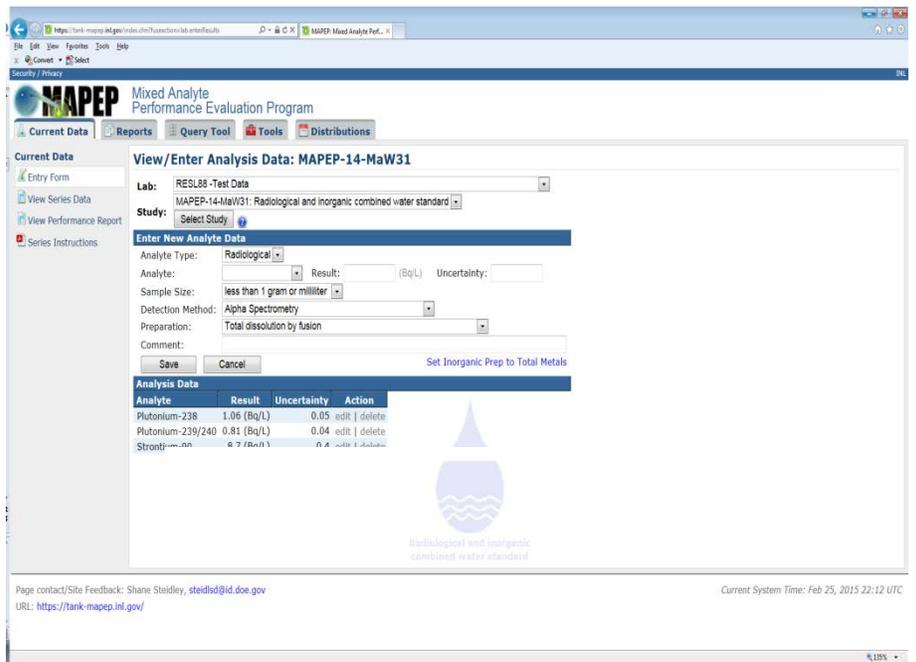
When users get to the shipping information, they may elect to check the “Same as Mailing Info” and/or “Same as Contact Info” to help provide information for shipping.

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.

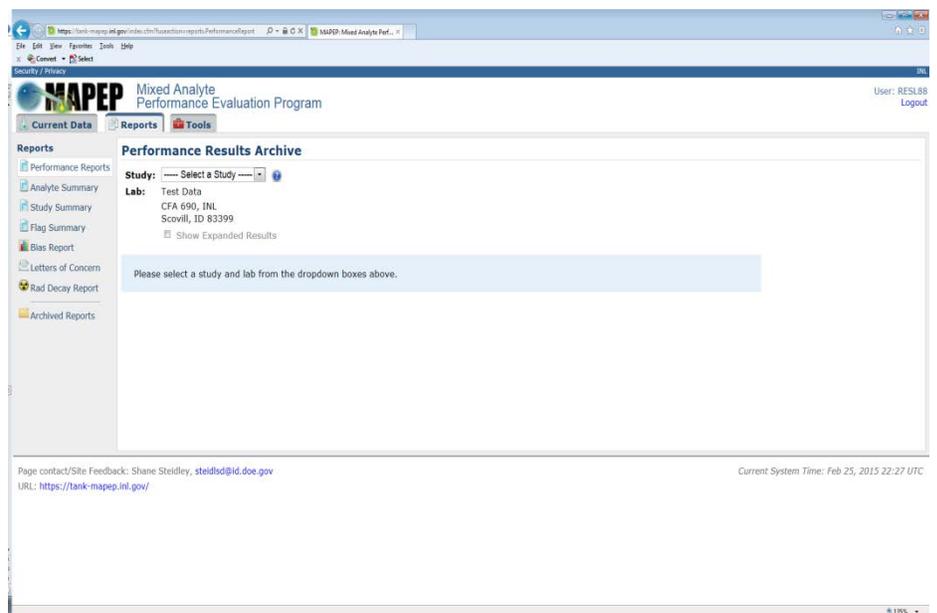
Select the appropriate analyte type (radiological, inorganic, semi-volatiles or pesticides) to start reporting data. The appropriate analyte list, units, and potential method codes are presented based upon the analyte type selected.



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 that gives you 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 laboratories PERFORMANCE REPORTS.

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 or vegetation. Finally, click the VIEW button to retrieve the analyte specific performance data.

**Laboratory Analyte Summary**  
 Analyte: Cesium-134  
 Study: All Studies

#	Study	Result	Ref Value	Flag	Notes	Bias (%)	Unc Value	Unc Flag	Units
1	MAPEP-12-RdV27	6.50	6.51	A		-0.2	0.27		(Bq/sample)
2	MAPEP-12-RdV26	8.52	8.43	A		1.1	0.35		(Bq/sample)
3	MAPEP-11-RdV25	0.07		A			0.03		(Bq/sample)
4	MAPEP-11-RdV24	5.40	5.50	A		-1.8	0.23		(Bq/sample)
5	MAPEP-10-RdV23	4.89	4.79	A		2.1	0.21		(Bq/sample)
6	MAPEP-10-RdV22	4.32	4.39	A		-1.6	0.18		(Bq/sample)
7	MAPEP-09-RdV21	0.09		A			0.05		(Bq/sample)
8	MAPEP-09-RdV20	4.00	3.40	A		17.6	0.19		(Bq/sample)
9	MAPEP-08-RdV19	5.24	5.5	A		-4.7	0.23		(Bq/sample)
10	MAPEP-07-RdV18	6.20	6.28	A		-1.3	0.26		(Bq/sample)
11	MAPEP-07-RdV17	6.18	6.2101	A		-0.5	0.27		(Bq/sample)

**Flags:**  
 NOTE: This page is intended to demonstrate historical performance. Users should review individual performance reports as needed to fully understand the performance flags assigned, but not necessarily detailed below.  
 A = Result acceptable  
 W = Result acceptable with warning  
 N = Result not acceptable  
 RW = Report warning  
 NR = Not Reported

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.

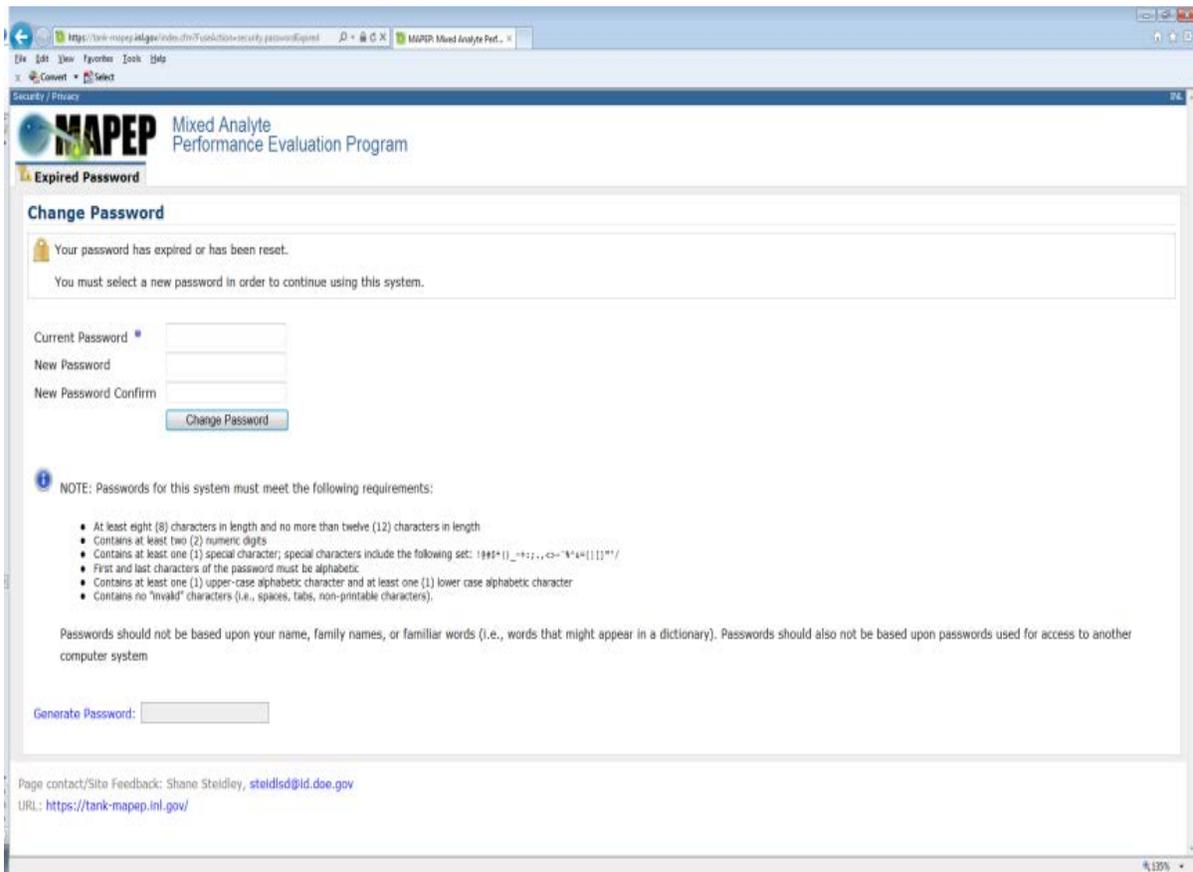
**Sample Statistical Summary**  
 Study: MAPEP-02-W10: Radiological and inorganic combined water standard  
 Radiological Reference Date: 12/01/2002

Analyte	T <sup>(1)</sup>	A <sup>(2)</sup>	Grand <sup>(3)</sup> Mean	Std Dev	Ref Value	Ref Unc	Acceptance Range
<b>Inorganic</b> Units: (mg/L)							
Antimony	34	33	0.254	0.025	0.241	0.001	0.169 - 0.313
Arsenic	17	17			<0.05		False Positive Test
Barium	36	34	0.755	0.031	0.756	0.004	0.529 - 0.983
Beryllium	33	33	0.791	0.037	0.802	0.004	0.561 - 1.043
Cadmium	17	17			<0.05		False Positive Test
Chromium	38	38	2.53	0.20	2.51	0.01	1.76 - 3.26
Copper	37	37	1.93	0.13	1.95	0.01	1.37 - 2.54
Lead	37	37	3.02	0.18	3.11	0.02	2.18 - 4.04
Nickel	37	37	2.12	0.13	2.16	0.01	1.51 - 2.81
Selenium	35	34	0.635	0.047	0.652	0.003	0.456 - 0.848
Silver	32						
Thallium	33	33	1.40	0.09	1.40		0.98 - 1.82
Uranium-235	2	2			9.19E-4		
Uranium-238	2	2			0.129	0.003	
Uranium-Total	5	5			0.130	0.003	
Vanadium	16	15			<0.1		False Positive Test
Zinc	37	37	2.46	0.16	2.46	0.01	1.72 - 3.20
<b>Organic</b> Units: (ug/L)							
Dieldrin	5	5					0
Heptachlor	5	5					0
1,2,4-Trichlorobenzene	22	22	35.4	8.0	35.4	3.5	11.3 - 59.5
1,2-Dichlorobenzene	21	20	37.5	8.0	37.5	3.6	13.6 - 61.5
1,3-Dichlorobenzene	21	20	40.3	7.7	40.3	3.4	17.1 - 63.5
2,4-Dimethylphenol	22	22	64.7	17.2	64.7	7.5	13.1 - 116.3
2,4-Dinitrotoluene	22	22	54.0	9.9	54.0	4.1	24.4 - 83.7

The MAPEP reporting system requires that passwords 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 following criteria for security reasons:

- At least 8 characters long
- Begin and end with letters
- Include two or more digits (e.g., 1, 2, 3 ...)
- Include one or more special characters (e.g., ! @ # % ^ & \* ...)
- Include a mix of both uppercase and lowercase letters.

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.



## **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 [MAPEP@id.doe.gov](mailto:MAPEP@id.doe.gov). Include your lab code/user id with all communications.

## Appendix G

### 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 PT standards use organic analytes in a separate soil and water PT standard.
- 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 that 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 traceable to NIST.
- MAPEP PT standards use real-world air filters and vegetation spiked with radionuclides that are traceable to NIST.
- Vendor certified standards for organic analytes are used if NIST traceable standards are unavailable.
- 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.

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- 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 material are verified with the same gamma-ray detectors and counting geometries that are 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 use refractory plutonium from time to time among the various test sessions and PT sample matrices. Refractory plutonium and its analysis is an important quality issue for DOE environmental programs and analytical performance.
- MAPEP PT standards will periodically use uranium in soil and other matrices that is difficult to dissolve. Front-end sample dissolution problems frequently lead to inaccurate and unreliable results, and acid-insoluble uranium is an important quality issue for DOE environmental programs and analytical performance.
- MAPEP PT standards incorporates antimony in soil and tests 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 the majority of other participants also choose a poor methodology and fail. This is especially true for refractory plutonium, antimony in soil,

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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, factors that 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 that 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, stable inorganic, and organic 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, stable inorganic, or organic master spiking solution that contains all targeted analytes for a given PT standard matrix will not be diluted or concentrated and used in a subsequent PT standard matrix.
- The variation in MAPEP PT standard complexity ensures that 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 that are 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 that 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 that can be used by gamma-ray spectrometry to make the measurement.

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## Measurement Traceability of PT Standards:

MAPEP reference values for the target analytes in the PT standards are 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: 1995, NIST Technical Note 1297, 1994, or other authoritative standard references.

- MAPEP PT standards use scientifically valid and legally defensible reference values with associated uncertainties and documented verification data according to ISO 17043 (see below).
- MAPEP PT standard results are evaluated with 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 will not be determined by the experimental analysis of the sample. Rarely, a radiological or stable inorganic reference value is derived from sample characterizations in accordance with ISO 17043. Reference values for organic analytes are derived from vendor certified standards, if NIST traceable standards are not available, and procedures that are used in accordance with ISO 17043 (see below).
- Total uncertainties for the reference values will not be determined empirically, but are determined 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 that involves a two-way exchange of material between RESL and NIST is used to demonstrate direct traceability of the analytical methods used by RESL for MAPEP PT material preparation and verification. RESL prepares material that is analyzed by NIST and RESL blindly analyzes material sent by NIST. All of the MAPEP PT matrices and radiological analytes are used in the two-way exchange. RESL is the only laboratory that utilizes a NIST RTP program.

**MAPEP utilizes the individual analytes that are listed in Appendix A of the MAPEP Handbook. There are 10 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 inorganics compounds.
2. Mixed Analyte Water (MaW) matrix. MAPEP uses naturally occurring water (well, sub-surface, surface, spring, river, lake, etc.) that has been 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. Organic Analyte Water (OrW) matrix. MAPEP uses water that contains no background organic compounds.

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4. Organic Analyte Soil (OrS) matrix. MAPEP uses soil that contains no background organic compounds.
5. Radiological analytes in a vegetation (RdV) matrix. MAPEP uses vegetation that is a naturally occurring grass-type matrix. The vegetation has been characterized for background radionuclide activities.
6. Radiological analytes in an air filter (RdF) matrix. MAPEP uses 47-mm glass fiber filters that have been characterized for background radionuclide activities.
7. Gross alpha/beta radionuclides in water (GrW) matrix. MAPEP uses naturally occurring water that has been characterized for background radionuclide activities.
8. Gross alpha/beta radionuclides in air filter (GrF) matrix. MAPEP uses 47-mm glass fiber filters that have been characterized for background radionuclide activities.
9. Radiological analytes in alkaline water (XaW) matrix. MAPEP uses naturally occurring water that has been characterized for background radionuclide activities.
10. Strontium-89 and Strontium-90 analytes together in an air filter (SrF) matrix. MAPEP uses 47-mm glass fiber filters spiked with Sr-89 and Sr-90 to test analytical methods for the determination of both strontium isotopes. Consequence management, among other groups, expressed a need for this matrix.

**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/Organic Analyte Concentrations:**

- Stable inorganic/organic analyte concentrations typically do not exceed the Resource Conservation and Recovery Act (RCRA) limits for hazardous material.
- The semi-volatile organic analyte concentrations are based on the NELAC Institute Performance Criteria Field of Proficiency Testing tables.
- 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

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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/organic analytes.

**False Positive/Negative Testing and Sensitivity Evaluations.** False positive/negative testing and sensitivity evaluations are used in radiological, stable inorganic, and organic 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 that 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 that is 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 that 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 that 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

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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 under estimating or over inflating their total uncertainties. If the total uncertainty is over inflated to try to pass a false positive test, it will result in a "Not Detected" if the test is actually a sensitivity evaluation, and vice versa for a false positive test. False negatives and failed sensitivity evaluations can also result from under estimating the total uncertainty. An accurate estimate of measurement uncertainty is required for consistent performance at the acceptable level.

### **Organic Analytes:**

Total uncertainties are not currently required for organic results; therefore, the radiological false positive/negative tests that use measurement uncertainty cannot be applied to organic analyses. Contamination, spectral interferences, retention time shift, and isomer misidentification are common causes of false positive/negative results for organic analyses.

- 1) MAPEP tests for false positive/negative organic results for each PT test session. MAPEP has determined that some analytical laboratories may not calibrate for all the components present in the target analyte list in U.S. EPA SW-846 Method 8270 "Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Capillary Technique". For this reason, MAPEP uses reported "less than" values to represent calibrated target components and empty result fields imply that these components are not part of the facilities normal calibration.
- 2) For the organics in water standards: a laboratory that does not report a target analyte whose concentration is known to be greater than the laboratory reported "less than" value will be issued a "False Negative" and "Not Acceptable" performance evaluation. A laboratory that reports results for a target analyte known not to be present, and other participants substantiate the analyte's absence, will be issued a "False Positive" and "Not Acceptable" performance evaluation.
- 3) For the organics in soil standards: a laboratory that does not report a target analyte whose concentration is known to be greater than the laboratory reported "less than" value, and other participants substantiate the analyte's presence, will be issued a "False Negative" and "Not Acceptable" performance evaluation. A laboratory that reports results for a target analyte known not to be present, and other participants substantiate the analyte's absence, will be issued a "False Positive" and "Not Acceptable" performance evaluation.
- 4) Misidentification of isomers (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene) will be flagged as "Not Acceptable".
- 5) Both high and low concentrations in an analyte category shall be included to evaluate if the

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participants analyze field samples at project-required dilutions. Excessive interference between closely eluted compounds of substantial concentration difference that requires unique or non-routine treatments shall not be used.

**PT Standard Verification:**

MAPEP shall verify the reference values for the MAPEP PT standards of each test session (Series) according to the ISO 17043 requirements 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 that 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.
- Organic Reference Value Verification:  
The PT sample composition shall be verified before utilization for the creation of PT standards. Initial verifications ensure that there are no gross errors in the PT standard production process and serve as a baseline for evaluation of laboratory performance. MAPEP organics shall use these guidelines to complete verification: verify the composition of the PT standard spiking solution for the water matrix or the prepared final soil standard with a definitive method typically used for proficiency testing (usually gas chromatographic mass spectrometry). Although the composition of the spiking solution for the PT water standards is well known, conduct initial verification to ensure that the mean measured concentrations +/- 10% of prepared values are analytically within acceptance ranges of analytical errors (including preparation and measurement errors).

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## **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 be based on ILAC G13:2000 and ISO 17043. 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. For the semi-volatiles, the phenolic compounds will be monitored for homogeneity, but shall not be a primary indicator for PT sample homogeneity due to their known reactivity and/or poor extraction efficiencies. 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

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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 ILAC G13:2000 and ISO Guide 43. 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.

**Stability testing for organic analytes:**

Organic compounds are stable for the length of the test session, but analyses must be performed in accordance with holding time requirements. Therefore, stability testing is not applicable for organic analytes.