

# Reference Sample an Alternative to Reference Material

Understanding measurement uncertainty to improve  
business certainty

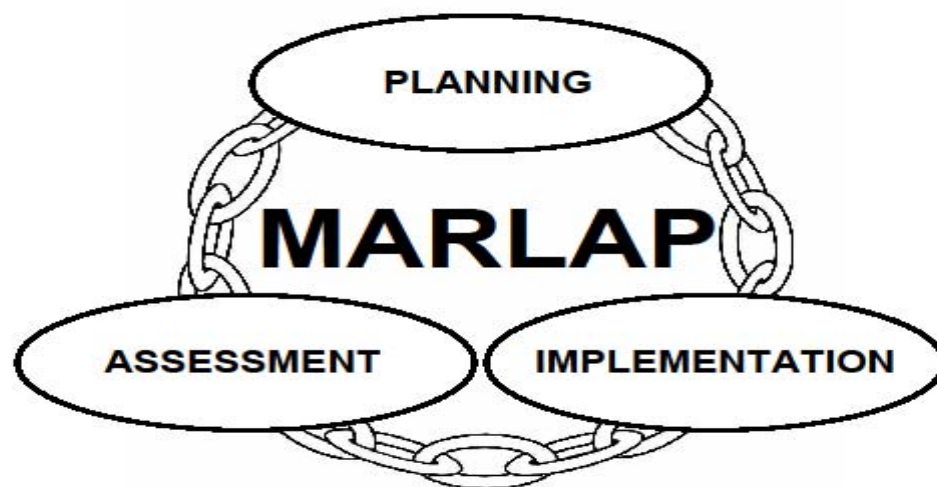
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NUREG-1576  
EPA 402-B-04-001A  
NTIS PB2004-105421



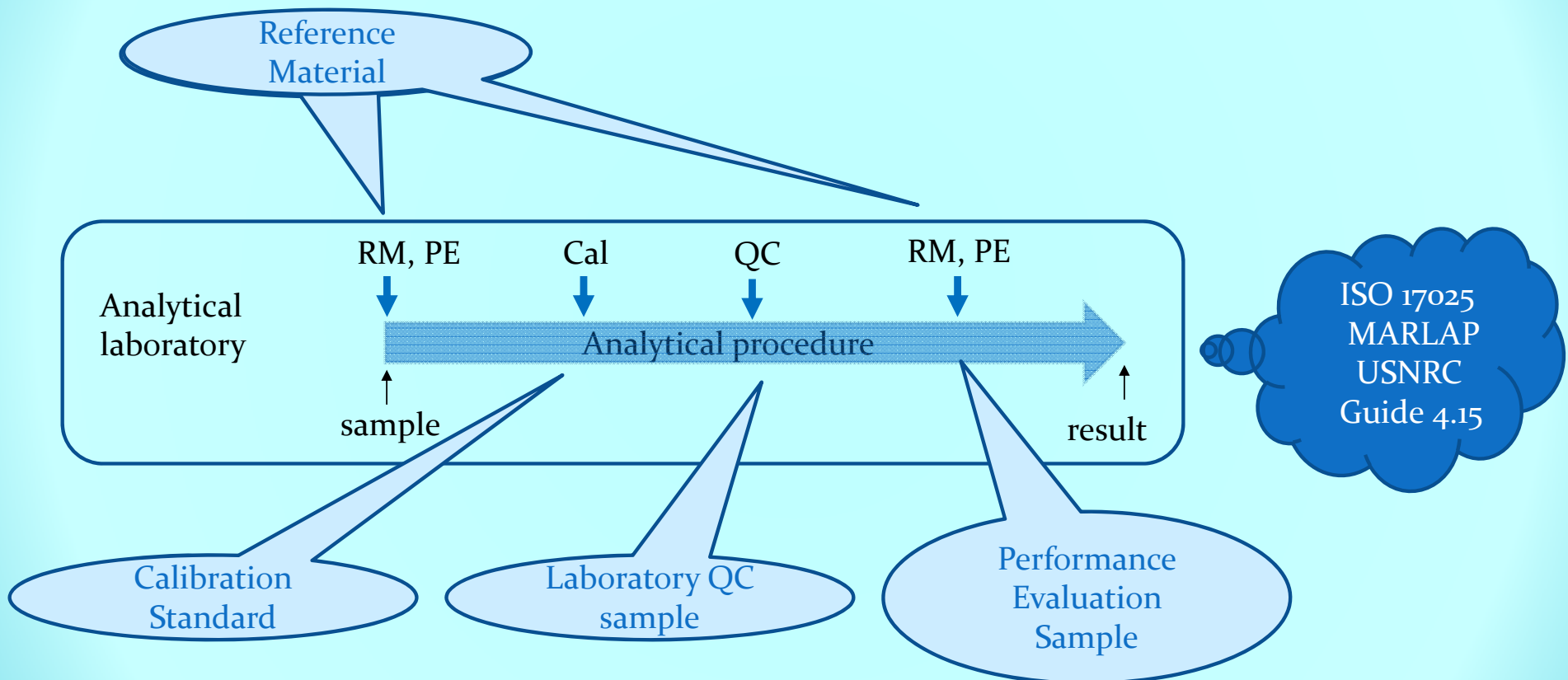
# Multi-Agency Radiological Laboratory Analytical Protocols Manual

Volume I: Chapters 1 – 9 and Appendices A – E



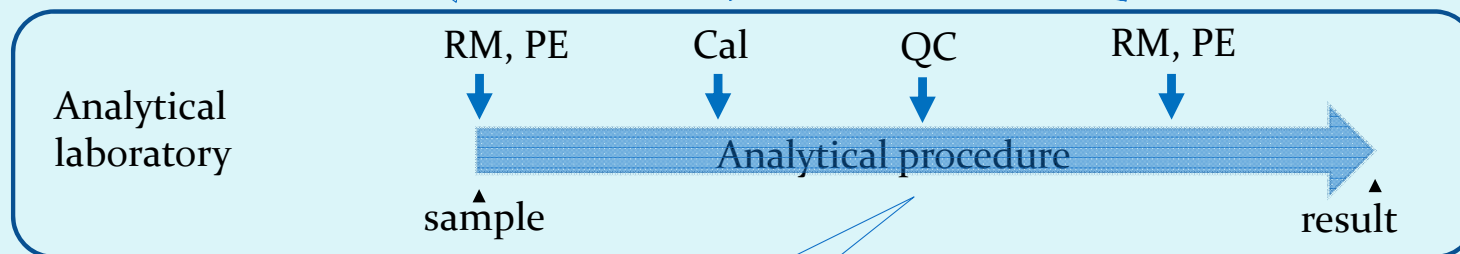
July 2004

“Laboratory data should be produced under a quality system that incorporates internal assessment of the work performed by the laboratory, including QC”



- [VIM3] 5.13 reference material
- *RM*
- material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in **measurement** or in examination of **nominal properties**
  
- [VIM3] 5.14 certified reference material
- *CRM*
- **reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceability, using valid procedures
  
- [VIM3] 5.1 measurement standard
- etalon
- realization of the definition of a given **quantity**, with stated **quantity value** and associated **measurement uncertainty**, used as a reference

[MARLAP] 18.4.4 Certified reference materials (CRMs) are well-characterized, stable, homogeneous materials with physical or chemical properties that are known within specified uncertainty limits. Laboratories that analyze CRMs can compare their performance to the certified concentration and uncertainty levels. CRMs are used for the calibration of an apparatus or the assessment of a measurement method.



CRMs can be used as internal laboratory QC samples to evaluate the ability of analytical methods to handle the matrix. CRMs need not be known to the analyst but can be introduced into the analytical stream as a blind. Comparison of analytical results of CRMs to their certified values provides linkage to the NIST radioactivity primary standards and a measure of method accuracy.

# PE/PT sample program

PE- performance evaluation

PT- proficiency testing

“evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons”

- Metrology organizations issue CRMs in various matrices with critically evaluated concentration values for the radionuclide constituents. A CRM issued by NIST or under license from NIST is called a “standard reference material” (SRM). The usefulness of a reference material depends on the characterization of the radionuclide source, activity levels, and their estimated uncertainties.
- The degree of equivalence in the analytical behavior of real samples and a CRM with respect to various measurement procedures (methods) is summarized in a concept called 'commutability of a reference material' (Preparation and Certification of Large-Sized Dried (LSD) Spike IRMM-10270, JRC 2013).



There are various definitions expressing this concept:

**[VIM] 5.15 commutability of a reference material** property of a **reference material**, demonstrated by the closeness of agreement between the relation among the **measurement results** for a stated **quantity** in this material, obtained according to two given **measurement procedures**, and the relation obtained among the measurement results for other specified materials

**[CLSI Guideline EP30-A]** recommends the use of the following definition for the term *commutability*:

"The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

## Available NIST Standard Reference Materials

SRM #	Name
4349	Nevada Soil (planned)
4350B	River Sediment
4351	Human Lung Powder
4352	Human Liver Powder
4353A	Rocky Flats Soil Number 2
4354	Lake Sediment Powder
4355	Peruvian Soil Powder
4356	Ashed Bone
4357	Ocean Sediment Powder
4359	Seaweed Radionuclide Standard
4360	Irish Sea Sediment (In preparation)

~300g of freeze-dry material in glass bottle  
Certificate Issued: November 2005

Reference Date: 01-Jan-2002  
Radionuclides certified:  $^{40}\text{K}$ ,  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ ,  $^{228}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$

24 Laboratories have participated in the Certification

11 methods were used for the certification

**IAEA Materials characterized for C-14**

Title	Category	Description	Release Date
<a href="#"><u>IAEA-C1</u></a>		Marble	1991-01-01
<a href="#"><u>IAEA-C2</u></a>		Travertine	1991-01-01
<a href="#"><u>IAEA-C3</u></a>		Cellulose	1991-01-01
<a href="#"><u>IAEA-C4</u></a>		Wood	1991-01-01
<a href="#"><u>IAEA-C5</u></a>		Wood	1991-01-01
<a href="#"><u>IAEA-C6</u></a>		Sucrose Out of stock!	1991-01-01
<a href="#"><u>IAEA-C7</u></a>		Oxalic Acid	1998-01-01
<a href="#"><u>IAEA-C8</u></a>		Oxalic Acid	1998-01-01
<a href="#"><u>IAEA-C9</u></a>		Wood	2004-01-01

## IAEA RMs - Organic Matrix

Title	Category	Description	Release Date
<a href="#">IAEA-MA-B-3-RN</a>	Animal Products	Fish Flesh !Out of stock!	1987-01-08
<a href="#">IAEA-414</a>	Animal Products	Fish	2006-01-10
<a href="#">IAEA-A-12</a>	Animal Products	Animal Bone	1983-01-01
<a href="#">IAEA-152</a>	Animal Products	Milk Powder !Out of stock!	1988-11-01
<a href="#">IAEA-447</a>	Moss-Soil	Natural and artificial radionuclides in moss-soil	2011-05-01
<a href="#">IAEA-446</a>	Seaweed	Baltic Sea Seaweed !new!	2013-02-01
<a href="#">IAEA-448</a>	Soil	Soil from oil field new!	2013-03-11
<a href="#">IAEA-437</a>	Mussel	Mussel from Mediterranean Sea	2010-08-01
<a href="#">IAEA-473</a>	Milk powder	Milk powder new!	2014-10-30
<a href="#">IAEA-154</a>	Animal Products	Whey Powder !Out of stock!	1988-01-11
<a href="#">IAEA-321</a>	Animal Products	Milk Powder !Out of stock!	1990-01-02
<a href="#">IAEA-156</a>	Vegetation	Clover	1991-01-01
<a href="#">IAEA-372</a>	Vegetation	Grass	2010-03-15
<a href="#">IAEA-330</a>	Vegetation	Spinach	2009-05-01

## IAEA – RMs Inorganic Matrix

Title	Category	Description	Release Date
<a href="#">IAEA-418</a>	Sea Water	Mediterranean Sea Water	2009-10-01
<a href="#">IAEA-443</a>	Sea Water	Irish Sea water	2012-03-01
<a href="#">IAEA-444</a>	Mineral	Gamma emitting radionuclides in soil Out of stock!	2010-03-01
<a href="#">IAEA-434</a>	Mineral	Phosphogypsum	2010-03-01
<a href="#">IAEA-445</a>	Water	Gamma emitting radionuclides in water !Out of stock!	2010-04-01
<a href="#">IAEA-RGK-1</a>	Ores	Potassium Sulfate	1987-01-01
<a href="#">IAEA-RGTh-1</a>	Ores	Thorium Ore	1987-01-01
<a href="#">IAEA-RGU-1</a>	Ores	Uranium Ore	1987-01-01
<a href="#">IAEA-312</a>	Soils	Soil	1991-01-01
<a href="#">IAEA-375</a>	Soils	Soil !Out of stock!	1994-01-08
<a href="#">IAEA-SL-2</a>	Sediments	Lake Sediment	1987-01-03
<a href="#">IAEA-313</a>	Sediments	Stream Sediment !Out of stock!	1991-01-01
<a href="#">IAEA-314</a>	Sediments	Stream Sediment	1991-01-02
<a href="#">IAEA-384</a>	Sediments	Fangataufa Sediment	2007-01-08
<a href="#">IAEA-385</a>	Sediments	Irish Sea Sediment	2008-01-11

- Are those Reference materials commutable for your purpose?

### Reference sample:

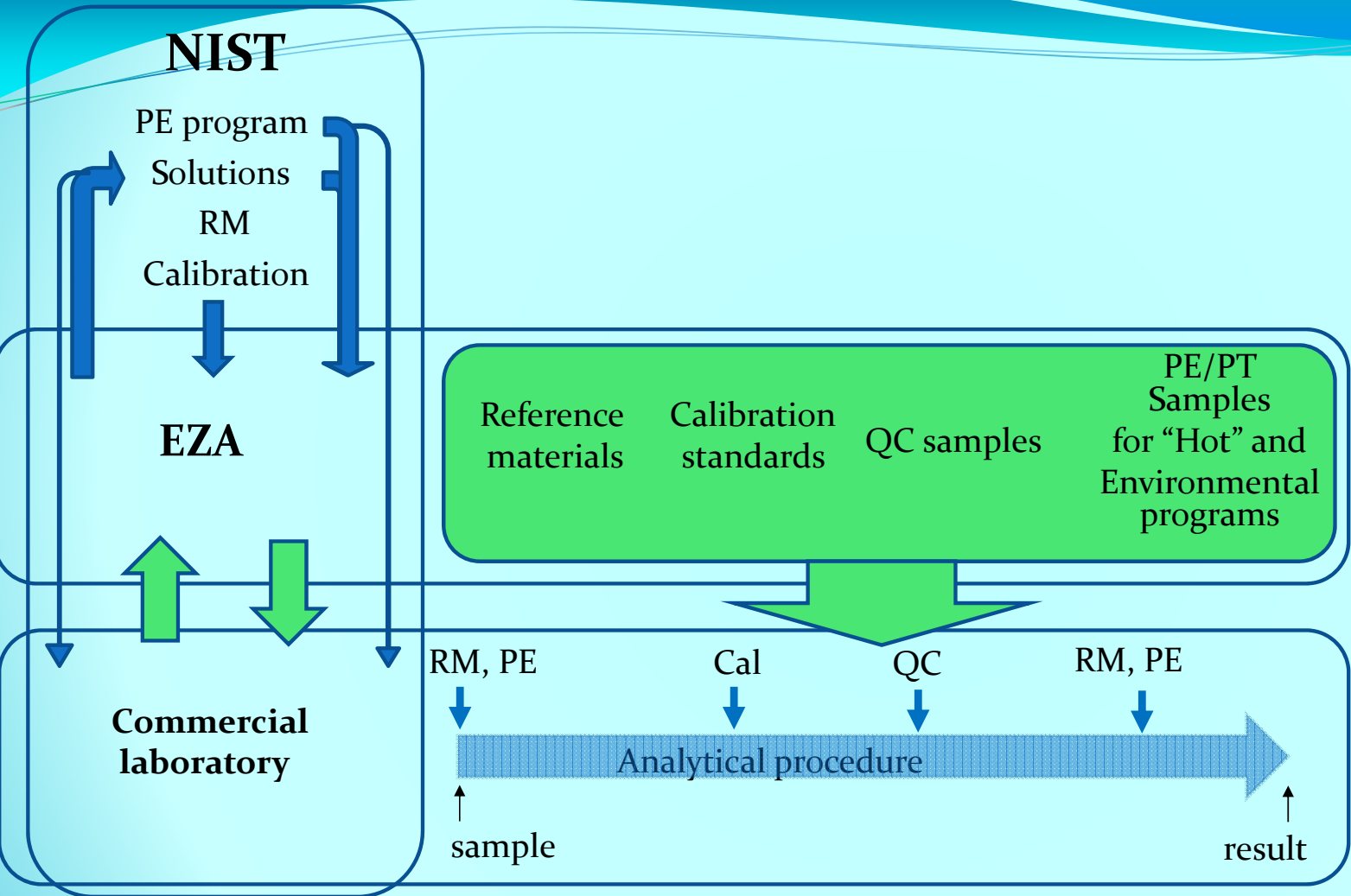
An artificial sample, created by spiking a “clean” material with radionuclides of known activities within specified uncertainty limits. Sample designed to be commutable and fit for the intended purpose in the measurement process.

RM	Parameter	RS
yes	Well-characterized	Yes for intended use
yes	Stable	Yes for intended use
yes	Homogeneous material	Can be, for intended use
yes	Certified activity	yes
yes	Specified uncertainty	yes
yes	Subsampling/Aliquoting	generally no
poor	Commutability	excellent
years	Time to develop	weeks
high	Cost of manufacturing	low

RM	Function	RS
Yes, limited	Use as a calibration standard Gamma spec, Gas Flow Counting, LS Counting, Alpha spec	Yes
Yes, limited	Use as Laboratory QC Sample	Yes
Yes, limited	Use as PT/PE sample	Yes
Yes, limited	Method development/validation/training	Yes
No	Use as a Tracer in Chemical Separation	Yes
No	Use as a Quench standard in LS	Yes



- Disadvantage of using RS
  - User (or provider of RS) has to ensure that spiked nuclides are contained by matrix and not absorbed by container material
  - User must ensure quantitative transferred of the sample from the container for further analysis
  - User must consider carefully the dissolution procedure to ensure complete isotopic exchange
  - With a few exceptions it will be not possible to provide organically bounded nuclides
  - Samples should be produced by certified body within proper regulatory requirements



ISO 17025, 17043  
ISO Guide 31,  
34 and 35  
ANSI N42.22  
CLIA

ISO 17025  
MARLAP  
USNRC Guide  
4.15

## EZA PE programs

- Hot Cross Check (HCC)– elevated activities
- Environmental Cross Check (ECC) – environmental levels

All PE samples are prepared and distributed for analysis as blind samples  
4 times a year:

HCC  
February  
May  
August  
November

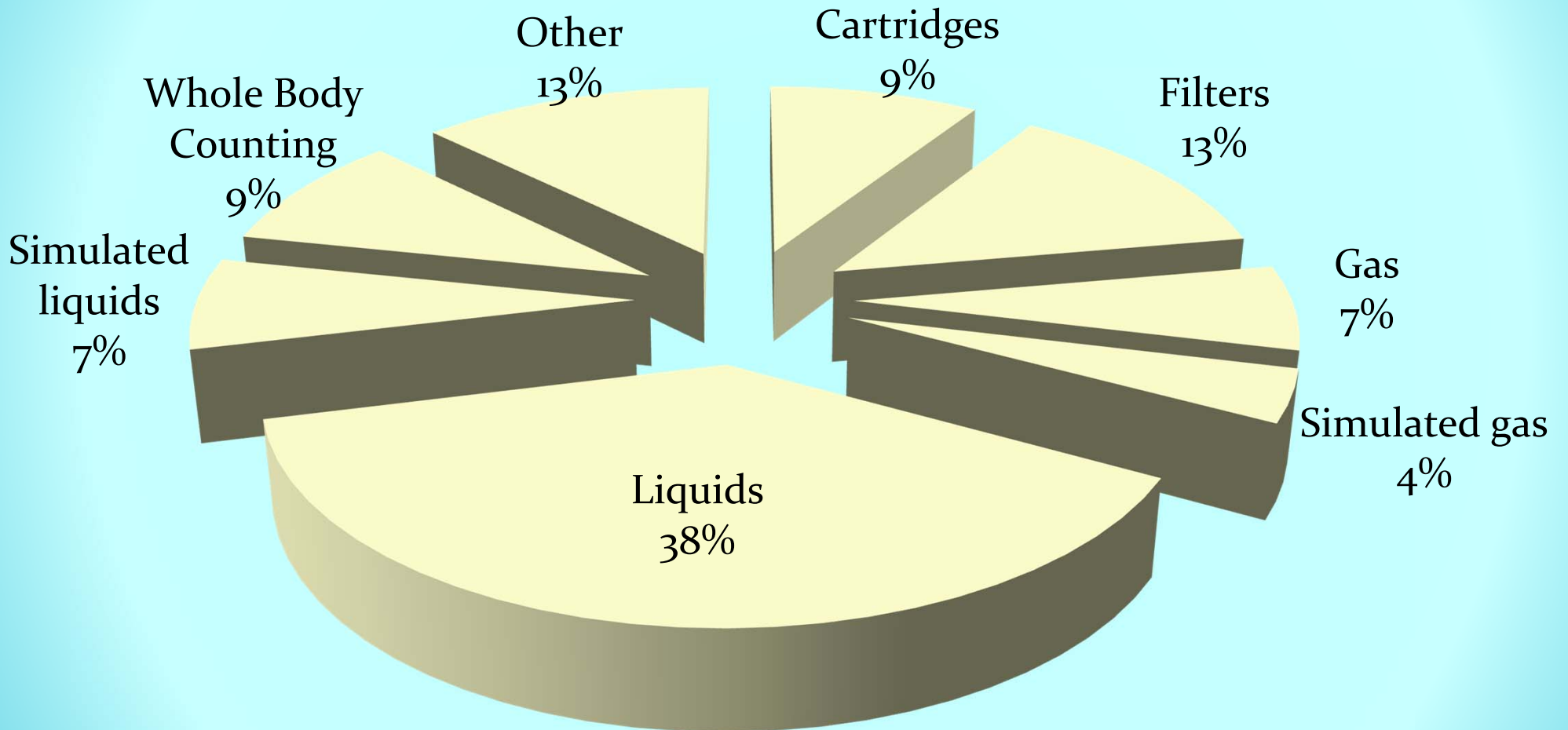
ECC  
March  
June  
September  
December

Customer results are evaluated and report is provided

## PE samples for Hot Cross Check (HCC) Program

- Liquids, Water: alpha, beta and gamma emitters (Simulated Activation Fission Mixture), transuranics,
- Simulated liquids: gamma emitters (Simulated Activation Fission Mixture),
- Soil (pulverized or sieved): alpha, beta and gamma emitters, transuranics,
- Air filters: alpha, beta and gamma emitters, natural activity, transuranics,
- Cartridges: I-131, other gamma emitters,
- Gas: Kr-85, Xe-127, Xe-133, Simulated Gas (mixed gamma emitters)
- U-235 fission mixture

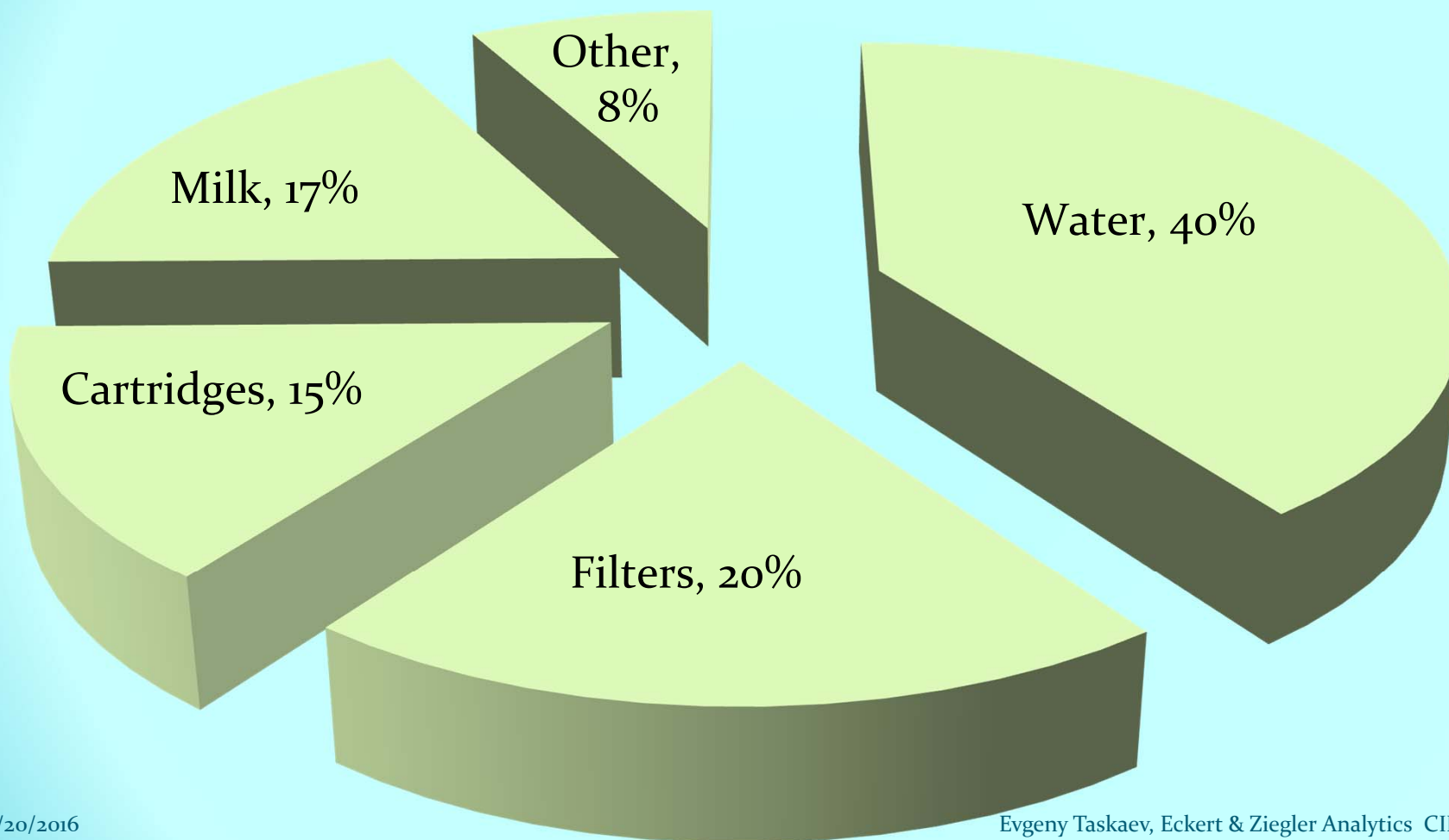
# Hot Cross Check Samples ~1200 per year



## PE samples for Environmental Cross-Check Program

- Water: alpha, beta and gamma emitters, natural activity, transuranics,
- Soil (pulverized or sieved): alpha, beta and gamma emitters, natural activity, transuranics,
- Air filters: alpha, beta and gamma emitters, natural activity, transuranics,
- Cartridges: I-131, other gamma emitters,
- Milk: I-131, Sr-89,90, gamma emitters,
- Synthetic or real urine, synthetic feces, ion exchange resin and other.

## Environmental Cross Check Samples ~350 per year



# RS vs RM ?

Thank you!