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A new role of Proficiency Testing in Nuclear Analytical Work

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In the beginning was the word..............
(Joh.1:1)

and the word was ***uncertainty***

- *but some people did not like it, and*
- *those who did could not use it, because we were not sure of its meaning*

International Vocabulary of Basic and General Terms in Metrology

VIM
2nd Edition
1993

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1. axiom

- A result

without statement of uncertainty

is useless

because no valid conclusions can be *reached*

Guide to the Expression of Uncertainty in Measurement

GUM
1st Edition
1995

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Evaluation of Sampling Uncertainty

- **Type A**

statistical analysis of actual observations

- **Type B**

any other method

2. axiom

- A result

with an incorrect statement of uncertainty

is dangerous

because erroneous conclusions may be reached

Accreditation after ISO 17025*

- Correct measurement results:
  - no significant bias
  - reliable uncertainty

*or ISO 15189

Proficiency Testing

ISO 13528:

Statistical methods for use in proficiency testing by interlaboratory comparisons

Laboratory Bias

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Measurand VIM 3

quantity *intended to be measured*

- *this definition differs from VIM 2*
- *must include exact specifications*

Definition of the Measurand I

- The *determinand, i.e.*

  the chemical species to be determined

- The *specified amount of material*

  to which the measurement should apply

Quantity value VIM 3

***Magnitude** of a quantity*

expressed as a product of
a number and a unit

Measurement Result VIM 3

Information on the measurand consisting of

- *a single **quantity value , y*** *and*
- *a **measurement uncertainty, u***

Definition of the Measurand II

- A result without corresponding definition of the measurand is worthless
- An uncertainty without corresponding specification of the measurand is misleading

Initial proficiency requirements I

1) Definition of the measurand, incl. identification of the determinand and specification of the system

2) Choice of analytical measurement method and detailing a procedure yielding traceable results

3) Development of an uncertainty budget, including correct application of counting statistics

4) Partial verification of uncertainty budget by replicate analyses

Final proficiency requirements II

5) *Choice of sampling strategy and number of samples to be analyzed*

6) *Reporting results of analyses corrected for bias and with specified coverage interval.*

7) *Final verification of analytical results and their uncertainties by proficiency testing*

8) *Calculation of the* E_n *number*

Our null hypothesis is now that

All reported measurement results for proficiency testing comply with these stipulations, so that

traceability is consistent with the definition of the measurand

all known biases have been corrected for

uncertainties are based on a verified uncertainty budget with a large number of effective degrees of freedom

Bayesian estimate of mean

$$\hat{\mu} = \frac{\sum_i \omega_i \cdot y_i}{\sum_i \omega_i}$$

where $\omega_i = u_i^{-2}$ *and* $u_\mu = \sqrt{\frac{1}{\sum_i \omega_i}}$

Test statistic

$$T = \sum_i \frac{(y_i - \hat{\mu})^2}{u_i^2}$$

Chi-square distribution
with n-1 degrees of freedom

E_n numbers

$$E_n^{(i)} = \frac{y_i - \hat{\mu}}{\sqrt{U_i^2 + U_\mu^2}}$$

$$U \sim 2u$$

“bottom up” strategy

a) expanded uncertainties, U, are converted to standard uncertainties, u = U/k

b) measurement results are ordered according to decreasing u

c) results are added in this order one at a time, and a value of T is calculated

d) if $T \leq \chi 2_{\alpha,m-1}$ *the next measurement result is added*

“bottom up” strategy

e) *if* $T > \chi 2_{\alpha,m-1}$ *the result with the largest contribution to T is removed*

f) *after reaching the end of the list go back to c) and add results previously removed*

g) *repeat c) to f) until there is no change in the selected group of measurement results*

h) *calculate the reference value* μ *and its uncertainty* u_{μ}

$\hat{\mu}$

“top down” strategy

*a)	apply robust algorithms A and S [3] to the y_i data for estimating μ, respectively their uncertainties U_i for estimating U_μ*

*b)	calculate E_n numbers and disregard all results with $|E_n|>1$,*

*c)	calculate the weighted mean of the remaining results, using $1/U_i^2$ as weights*

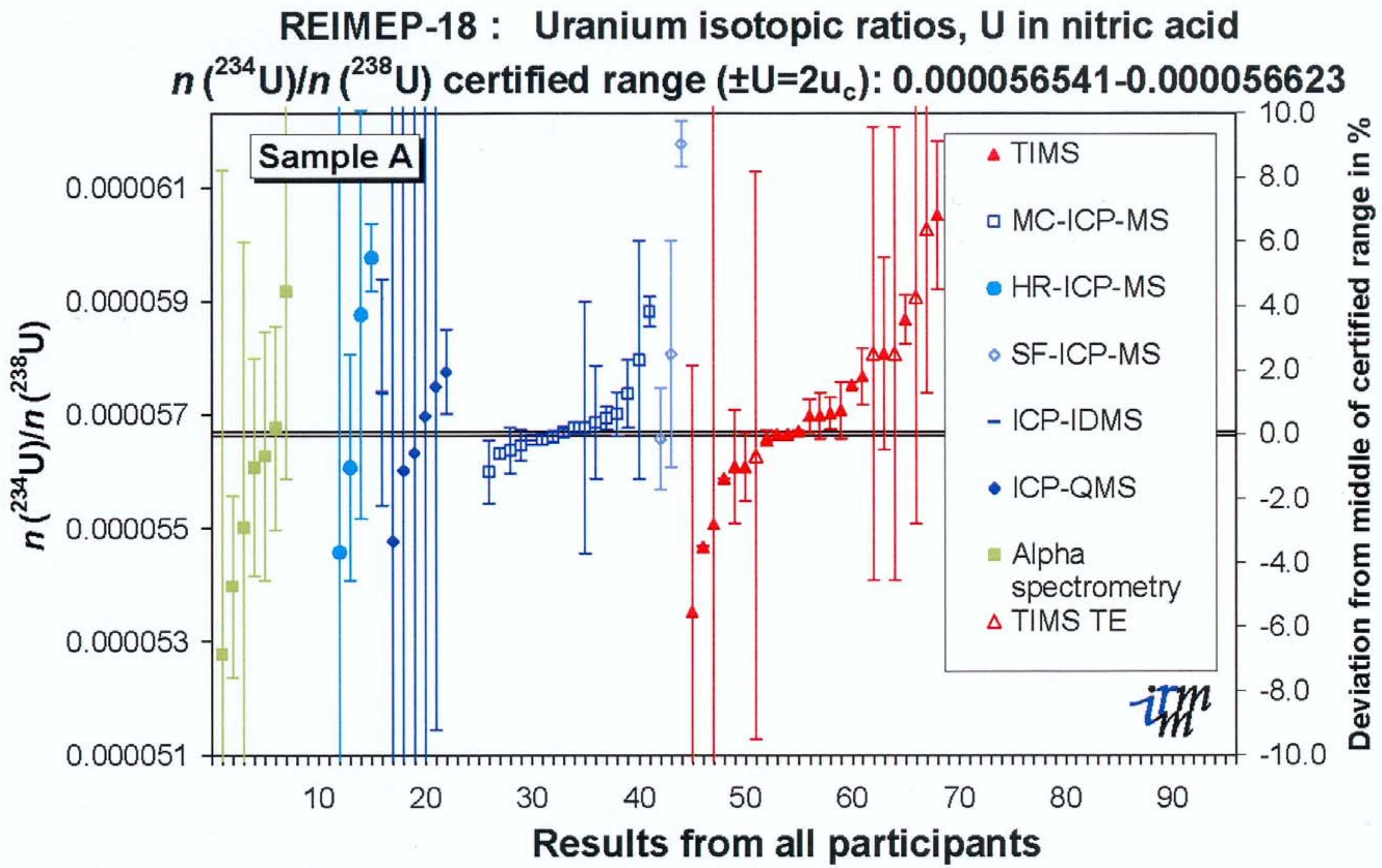
“top down” strategy

d) *calculate its corresponding uncertainty from*

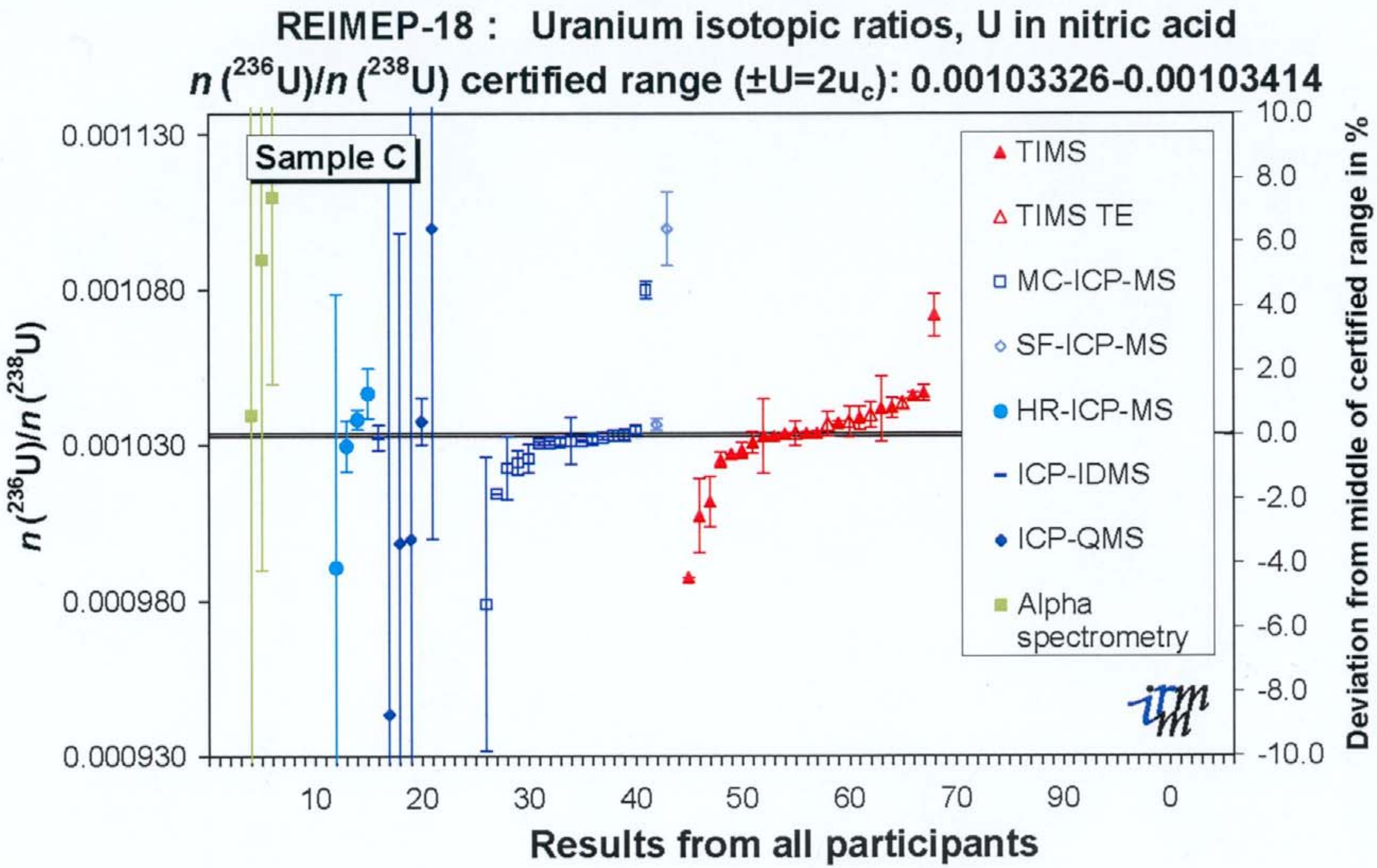
$$U_\mu^{-2} = \sum U_i^{-2}$$

e) *repeat b) to d) until there is no change in the selected group of measurement results*

f) *use their weighted mean as reference value and* U_μ *as its expanded uncertainty.*



Results for the $n(^{234}U)/n(^{238}U)$ ratio for REIMEP 18 A



Results for the $n(^{236}U)/n(^{238}U)$ ratio for REIMEP 18 C

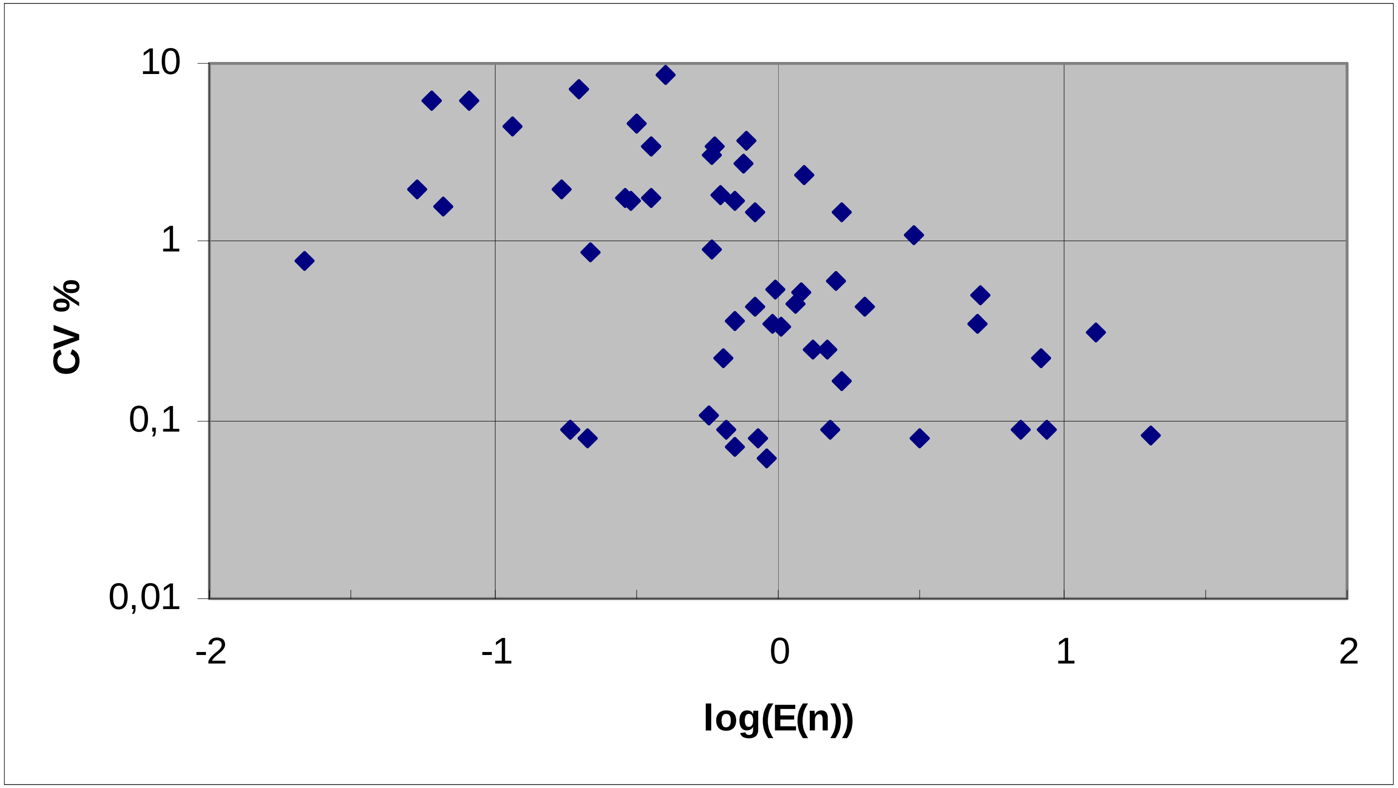
Reference values for Uranium isotopic ratios

Strategy	$^{234}U/^{238}U$ value ±Uncertainty (k=2)	Results accepted	$^{236}U/^{238}U$ value ±Uncertainty (k=2)	Results accepted
Bottom up	0.000056581±31	42	0.00103368±51	27
Top down	0.000056609±37	39	0.00103390±54	25
Combined	0.000056581±31	42	0.00103368±51	27

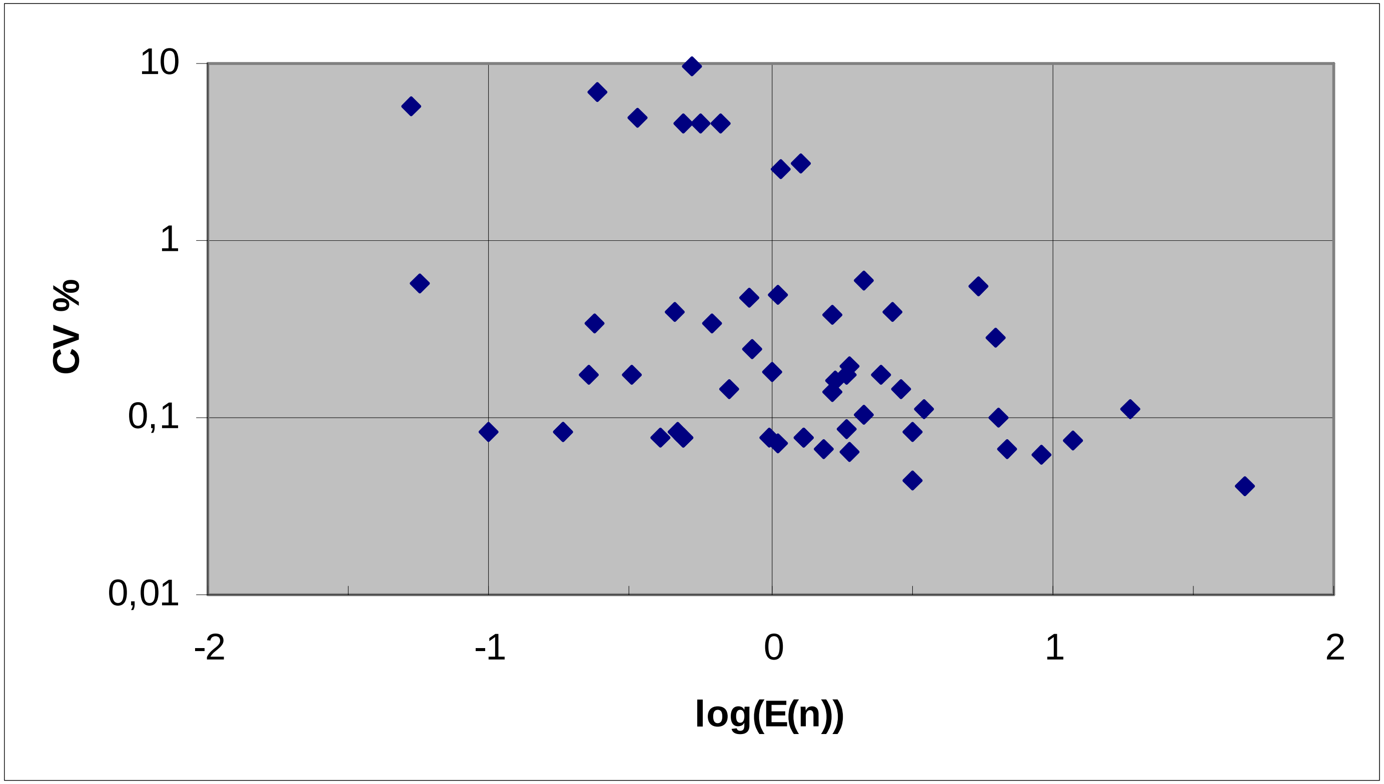
Correct measurement results

- Participants
- Methods

$^{234}U/^{238}U$ proficiency data



$^{236}U/^{238}U$ proficiency data



Median of E_n numbers for analytical methods

Technique	Sample A Median	Number results	Sample C Median	Number results
Alpha	-0,31	7	0,56	3
HR-ICP	0,20	4	0,59	4
ICP-IDMS	0,36	1	-0,32	1
ICP-QMS	-0,01	6	-0,24	5
MC-ICP	0,14	16	-1,06	16
SF-ICP	0,71	3	3,70	2
TE	0,35	5	1,45	4
TIMS	0,66	19	0,34	20

VIM 3 is a major challenge in

- Our way of interpreting analytical data

Co-operate with the client to define fitness for purpose

- Our way of treating proficiency data

Accreditation authorities beware of the uncertainty of assigned values

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Question from the audience:

- Would the proposed method lead to substantially different E_n numbers?

- Not for the particular example used here, but for the example used in ISO 13528 the drastic reduction of the uncertainty of the reference value greatly increases the detection capability for too optimistic reported uncertainties.

Comparison with certified values

Value	$^{234}U/^{238}U$ value ±Uncertainty (k=2)	Results accepted	$^{236}U/^{238}U$ value ±Uncertainty (k=2)	Results accepted
Reference	0.000056581±31	42	0.00103368±51	27
Certified	0.000056582±41	Sample A	0.00103370±44	Sample C

Reference values* for Pb in IMEP-9

Method	Reference value ± Uncertainty	Number of accepted results	Comment
Synthesis of Precision	617.7 ± 2.7	60	Recommended
E_n numbers	614.1 ± 3.2	59	Alternative
Robust average	605 ± 26	181	ISO 13528 (2005)
ICP-MS	623 ± 13	6	Certified value

***in units of 10^{-10} mol/L**