Polonium $\equiv$ 1st radioactive element discovered (1898)

A Tribute to the Discoverer

Happy 148th Birthday, Marie
7 November 2015

Polonium

solution stability

R. Collé -- NIST

Radioactivity Group Talk

25 November 2015

^{209}Po at NBS / NIST

Since Feb 2014 talk

1990 -- polonium solution stability	R. Collé, *Radioact. Radiochem*. **4**, no.2, 20-35 (1993).
1993 -- ^{209}Po SRM 4326	R. Collé, Z. Lin, et al., *J. Res. Natl. Inst. Std. Tech*. **100**, 1-36 (1995).
1994 -- ^{209}Po decay scheme	F.J Schima and R. Collé, *Nucl. Instrum. Meth, Phys. Res.* **A369**, 498-502 (1996).
1994 -- ^{205}Pb delayed isomeric state / LS implications	R. Collé, Z. Lin, et al., *Appl. Radiat. Isotop.* **45,** 1165-1175 (1994).
2005 -- ^{209}Po SRM 4326 recertification	R. Collé, L. Laureano-Perez , et al. [Certificate]
2005 -- ^{209}Po half-life discrepancy	R. Collé, L. Laureano-Perez, et al., *Appl. Radiat. Isotop*. **65,** 728-730 (2007).
2006 -- ^{210}Pb SRM 4337	L. Laureano-Perez, R. Collé, et al., *Appl. Radiat. Isotop*. **65,** 1368-1380 (2007).
2007 -- ^{209}Po & ^{210}Pb std methodology	R. Collé, L. Laureano-Perez, LSC 2008, Radiocarbon, 2009, pp.77-85
2008 -- ^{210}Pb intercomparison (NPL)	R. Collé, L. Laureano-Perez, LSC 2008, Radiocarbon, 2009, pp.77-85
2013 -- New ^{209}Po standardization method	R. Collé, R. Fitzgerald, L. Laureano-Perez, *J. Res. NIST* **120**, 138-162 (2015)
2013 -- ^{209}Po SRM 4326a	R. Collé, L. Laureano-Perez, *J. Res. NIST* **120**, 138-162 (2015)
2013 -- ^{209}Po definitive half-life	R. Collé, R. Fitzgerald, L. Laureano-Perez, *J. Phys. G*. **41,** 1051103 (2014)
2015 -- Critique Pommé ^{209}Po half-life	R. Collé, A. Collé, *J. Radioanal Nucl. Chem , DOI .. (2015)*
2015 -- Po solution stability	R. Collé, R. Fitzgerald, L. Laureano-Perez

Po Solution Stability

Belief in 1990

Po solutions at trace concentrations, under various alkaline, neutral,, or weakly acidic conditions are known to be unstable: being readily hydrolyzed, chemically deposited, or volatilized,; exhibiting “radiocolloidal” behavior; and undergoing “plate-out” or adsorption onto glass surfaces.

Stored Po solutions are generally considered by NIST to be stable in the acid range of 0.1 to 1.0 normality, but scant data exist on any possible long-term effects , particularly for very dilute, carrier free, aged solutions.

c. 1990 Collé study

(indebted to Jim Noyce for his meticulous records)

Carrier-free ^{208}Po and ^{210}Po solutions with "known" massic activity re-assayed after aged storage in flame-sealed glass ampoules storage

Number solutions studied	11
Range of solution ages	(1.2 to 8.8) years
Range of HCl normality	(0.09 to 2.0) mol/L
Range of massic activity	(< 0.1 to 3600) Bq/g
Range of recoveries found	(< 0.1 to 1.03) %
Typical recovery uncertainty (k = 1)	> 20 % at 0.1 Bq/g 1.2 % at 200 Bq/g

If 1 is Good;
2 is Better

Conclusions

< 0.3 mol/L – "clearly unstable"

0.3 to 0.5 mol/L – "somewhat equivocal"

$\geq$ 1 mol/L – "appear to be stable over many years approaching a decade"

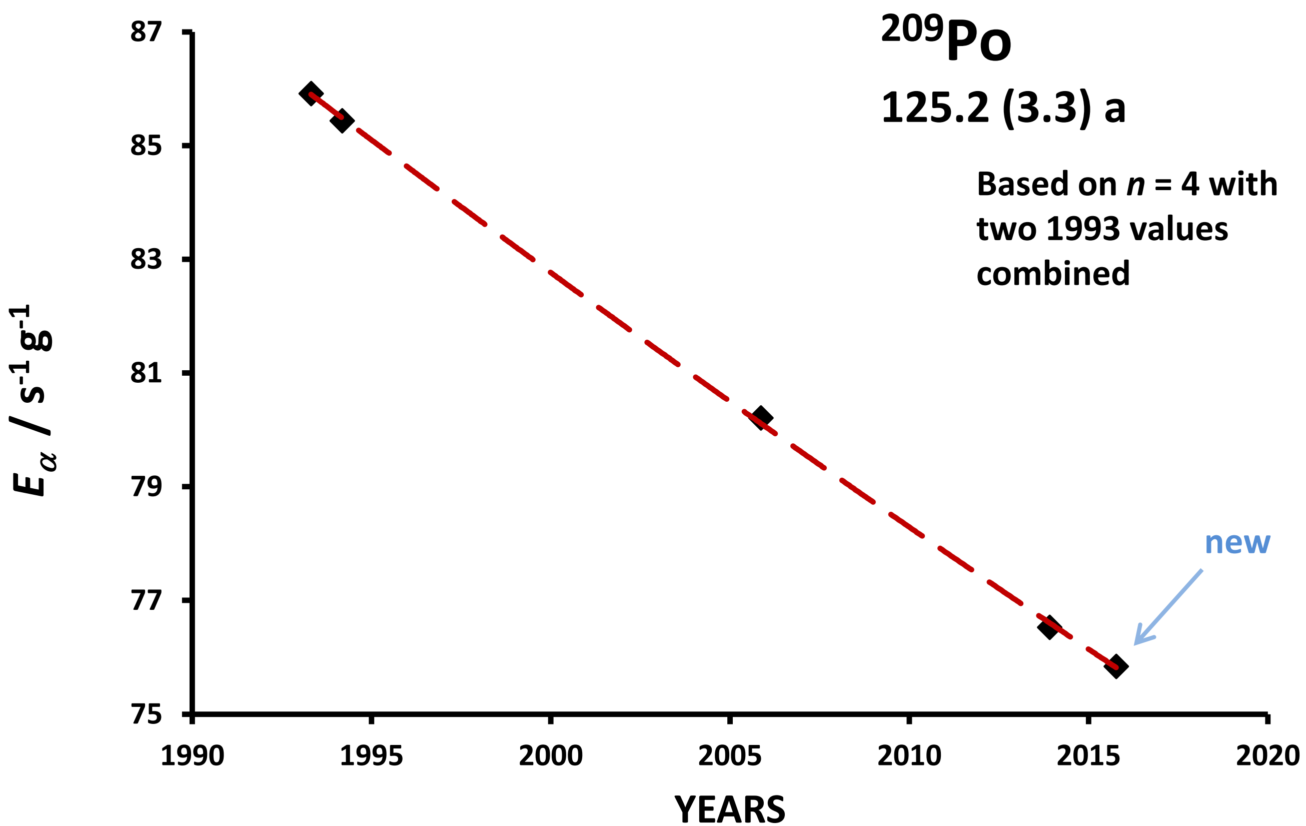
Therefore use 2 mol/L

R. Collé, *Radioact. Radiochem*. **4**, no.2, 20-35 (1993).

Half-life determination by decay

ASSUMED stability of the stored

<u>CARRIER-FREE</u> solutions over 20+ years



N.B. *each plotted value based on multiple measurements. Including present 2015 results, 34 data sets over a period of 22.6 years, with 744 LS measurements on 61 counting sources*

Carrier-free in 2 mol•L^{-1} HCl

Per gram of solution

4.32 (10^{11}) atoms of Po

1.20 (10^{21}) atoms of Cl

3.34 (10^{22}) molecules of H_2O

Po in solution is 1 part in 77 billion parts of H_2O ....

put in perspective

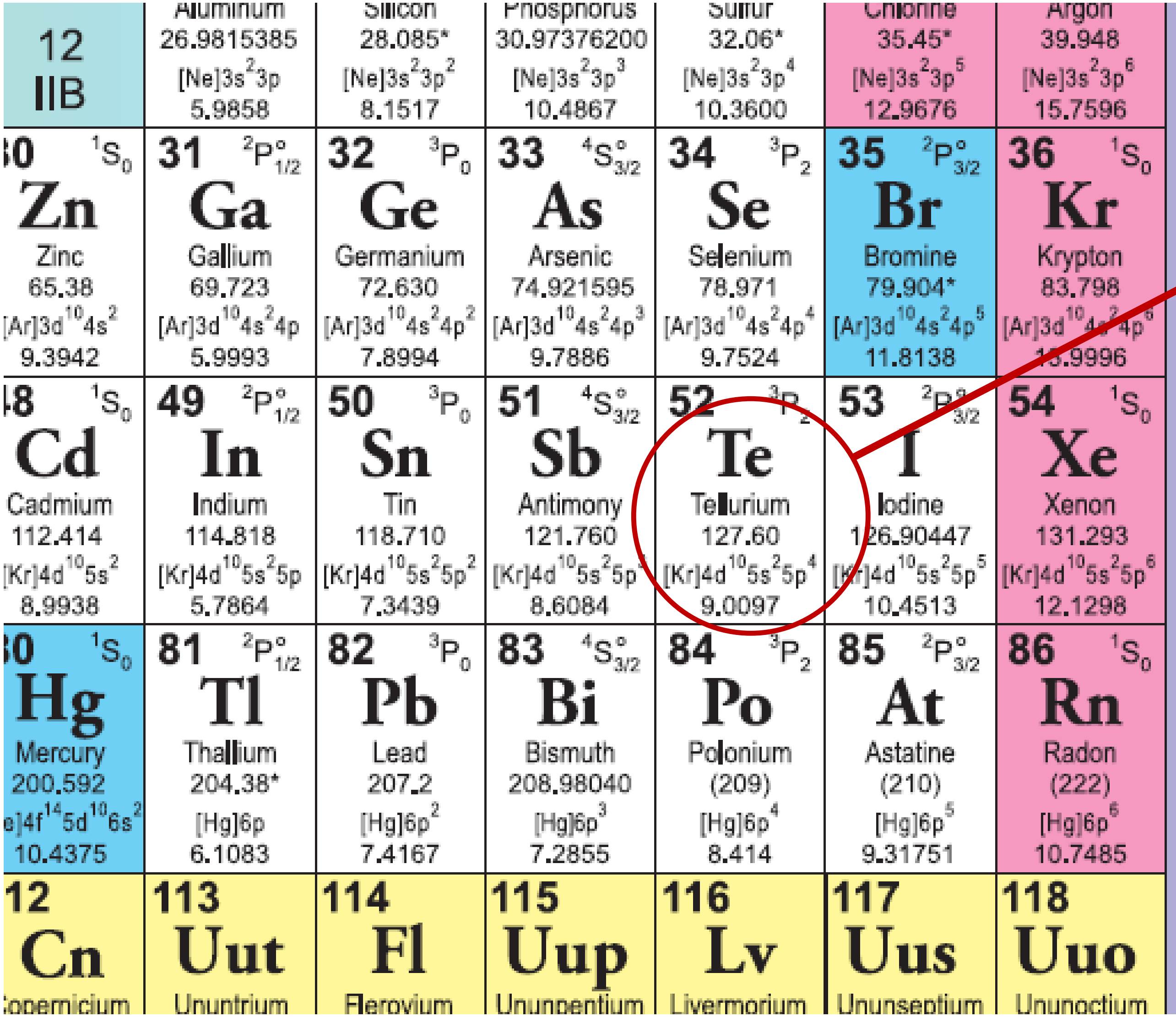
me

compared to

10 times

total world population

CARRIER
FREE
SOLUTION
APPEARS
TO BE
VERY
STABLE

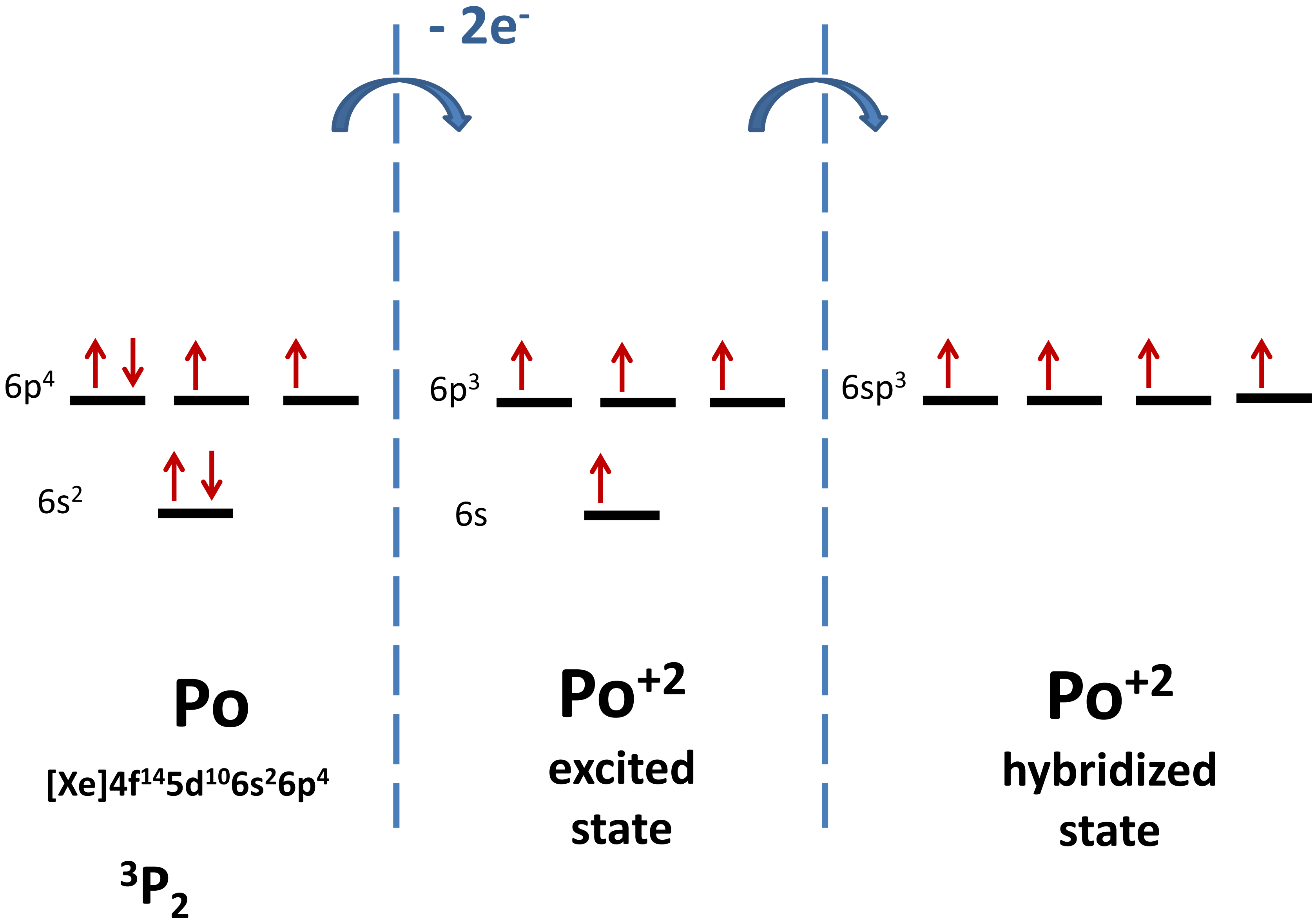


Not good Homolog

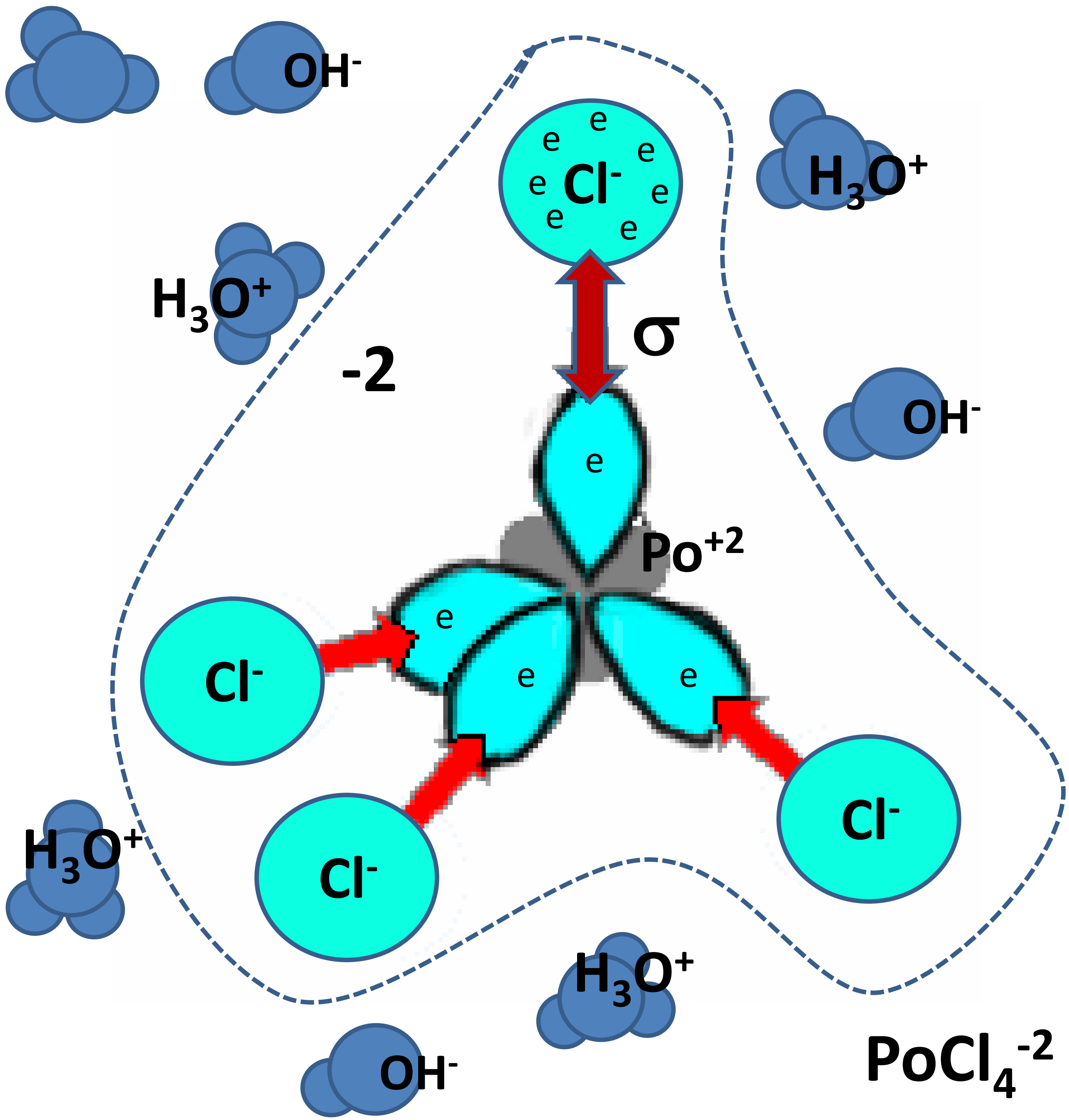
Most common oxidation states are +6 +4 -2

Most common oxidation state for Po is +2 with sp^3 hybridization (other states are rare)

NPL Experience



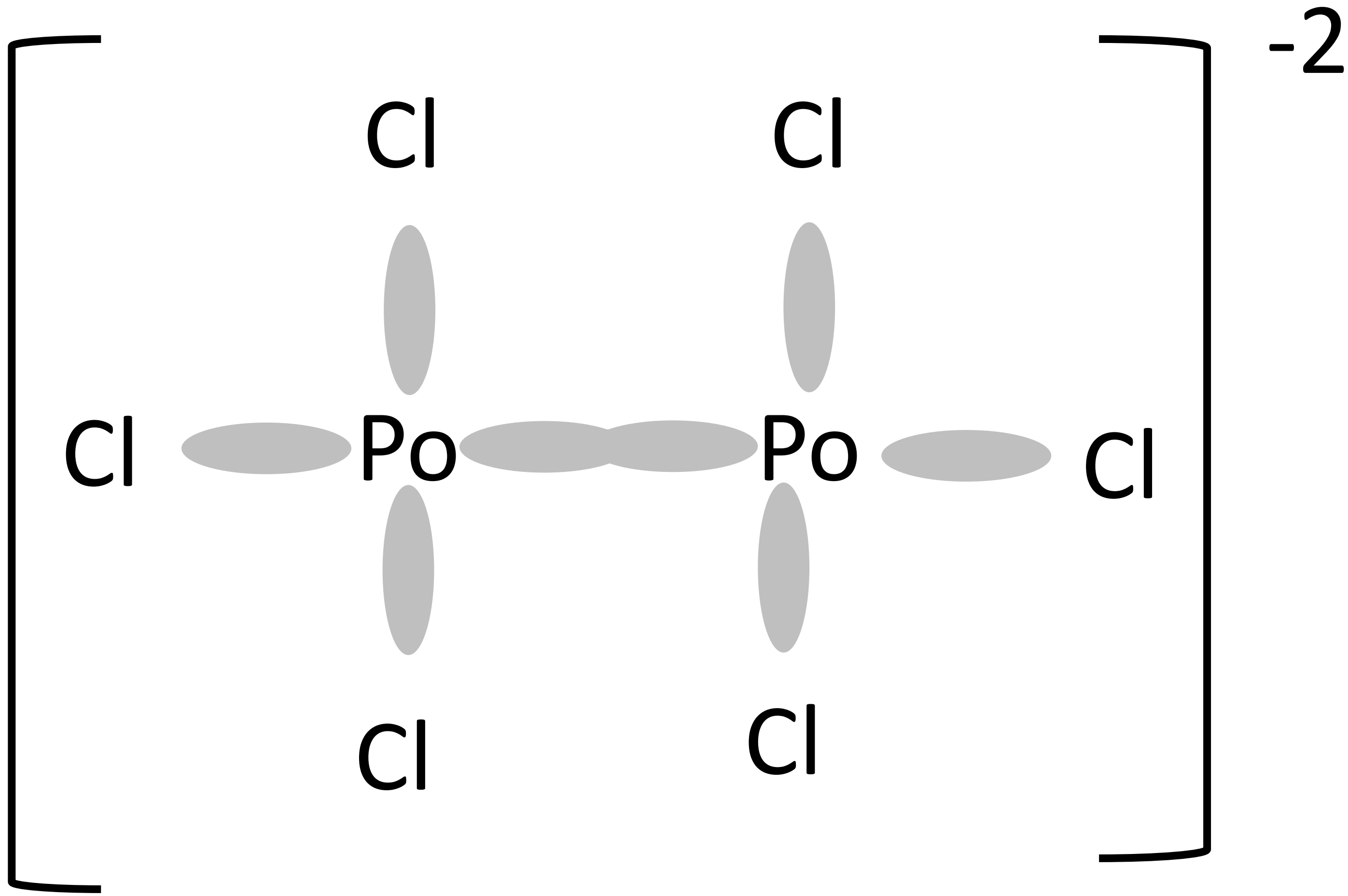
- 2e⁻
6p⁴
6s²
6p³
6s
6sp³
Po
[Xe]4f¹⁴5d¹⁰6s²6p⁴
³P₂
Po⁺²
excited state
Po⁺²
hybridized state



$$HCl + H_20 \rightleftharpoons Cl^- + H_30^+$$

$$H_20 + H_20 \rightleftharpoons OH^- + H_30^+$$

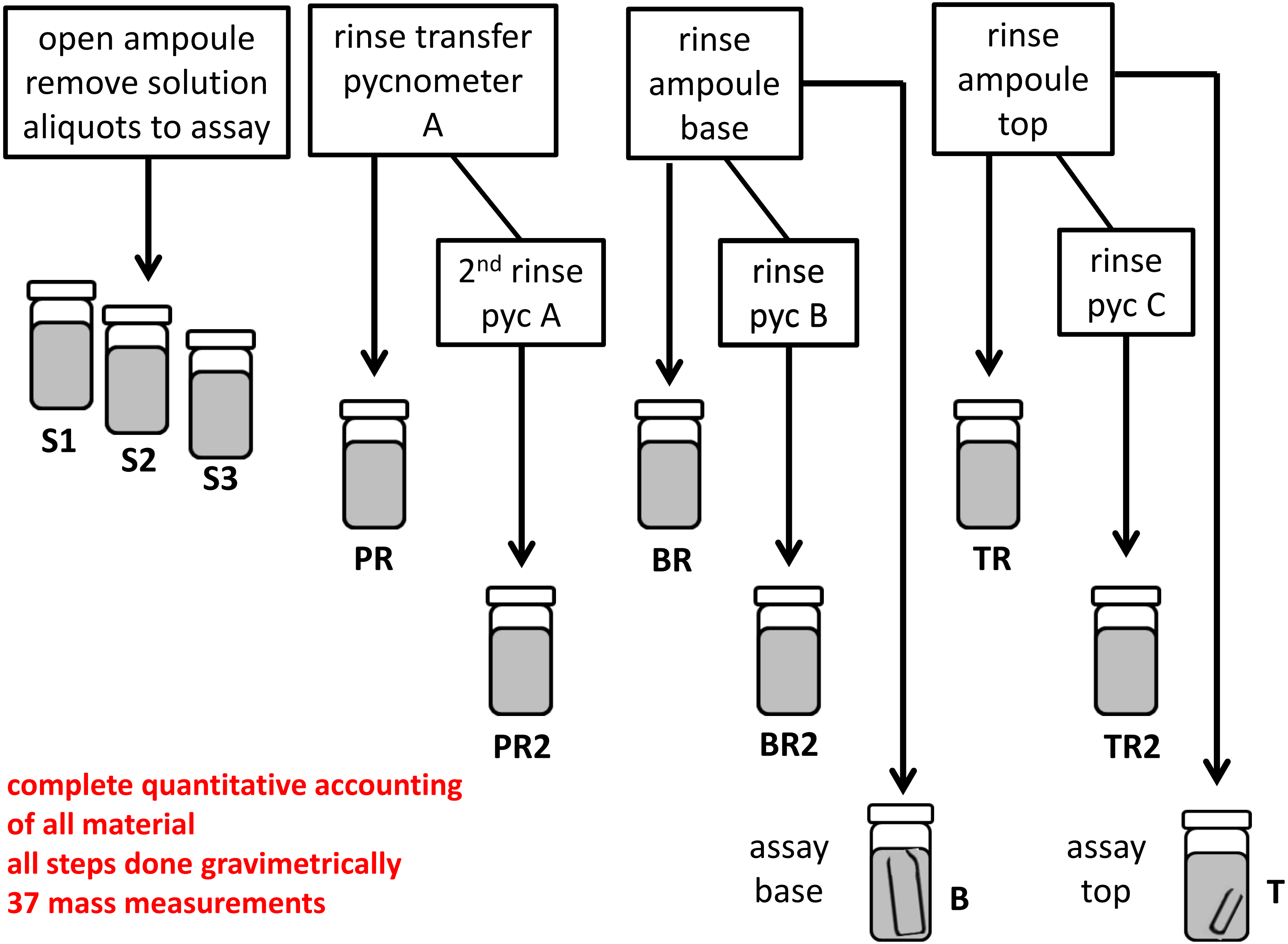
or
maybe
bigger



or maybe even bigger

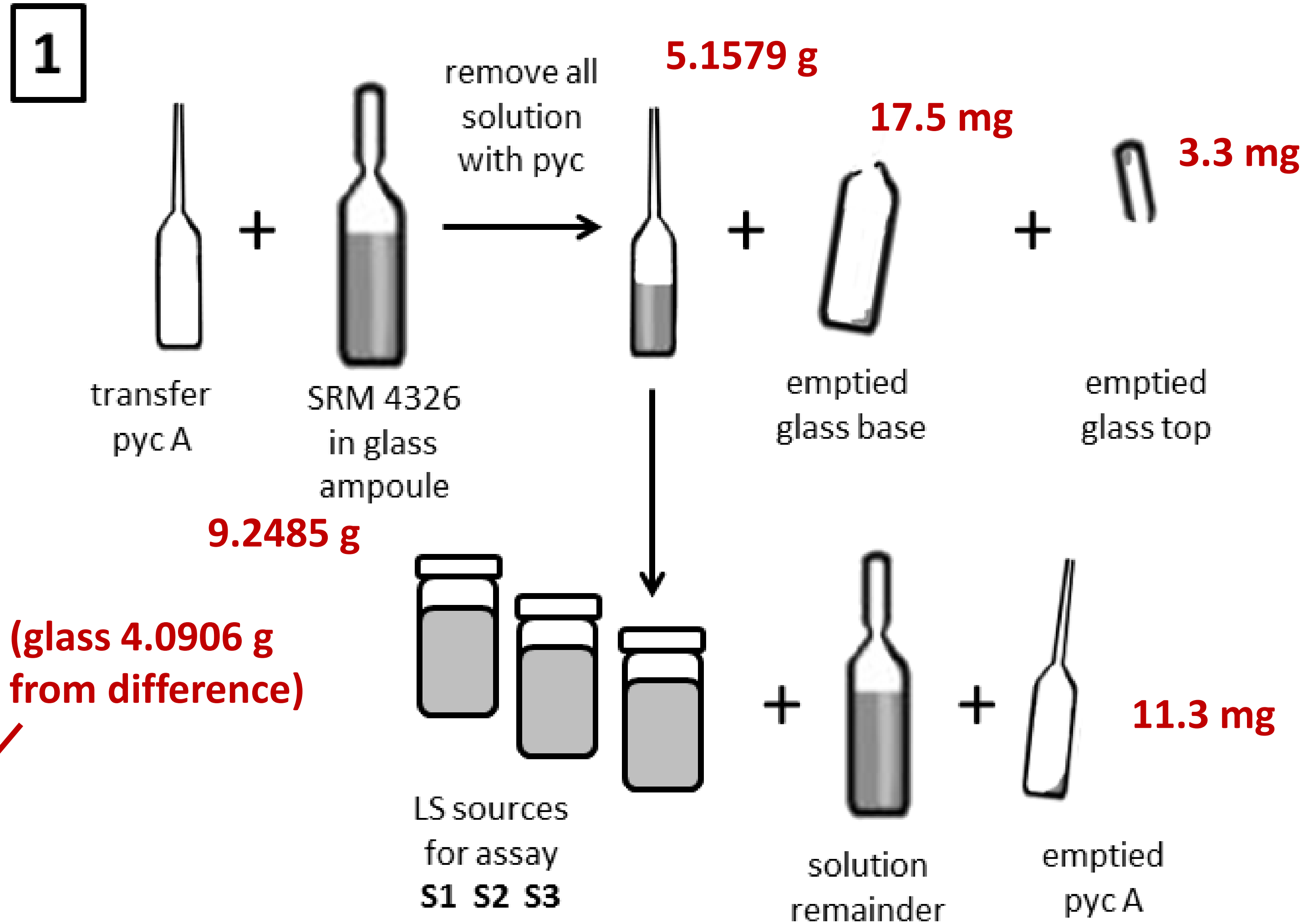
ampoules of SRM 4326

EXPT	ampoule id	solution mass (g)	sealed	opened	age (a)	
1	# 183 R	1.81	20 Nov 2013	17 Sept 2015	1.82	different procedure
2	# 146 R	3.09	7 Nov 2005	24 Sept 2015	9.88	dirty ampoule
3	# RX3	5.14	8 March 1993	7 Oct 2015	22.42	original ampoule
4	# 40 R	2.70	24 Feb 1994	26 Oct 2015	21.67	



- complete quantitative accounting of all material
- all steps done gravimetrically
- 37 mass measurements

Empty the ampoule & assay

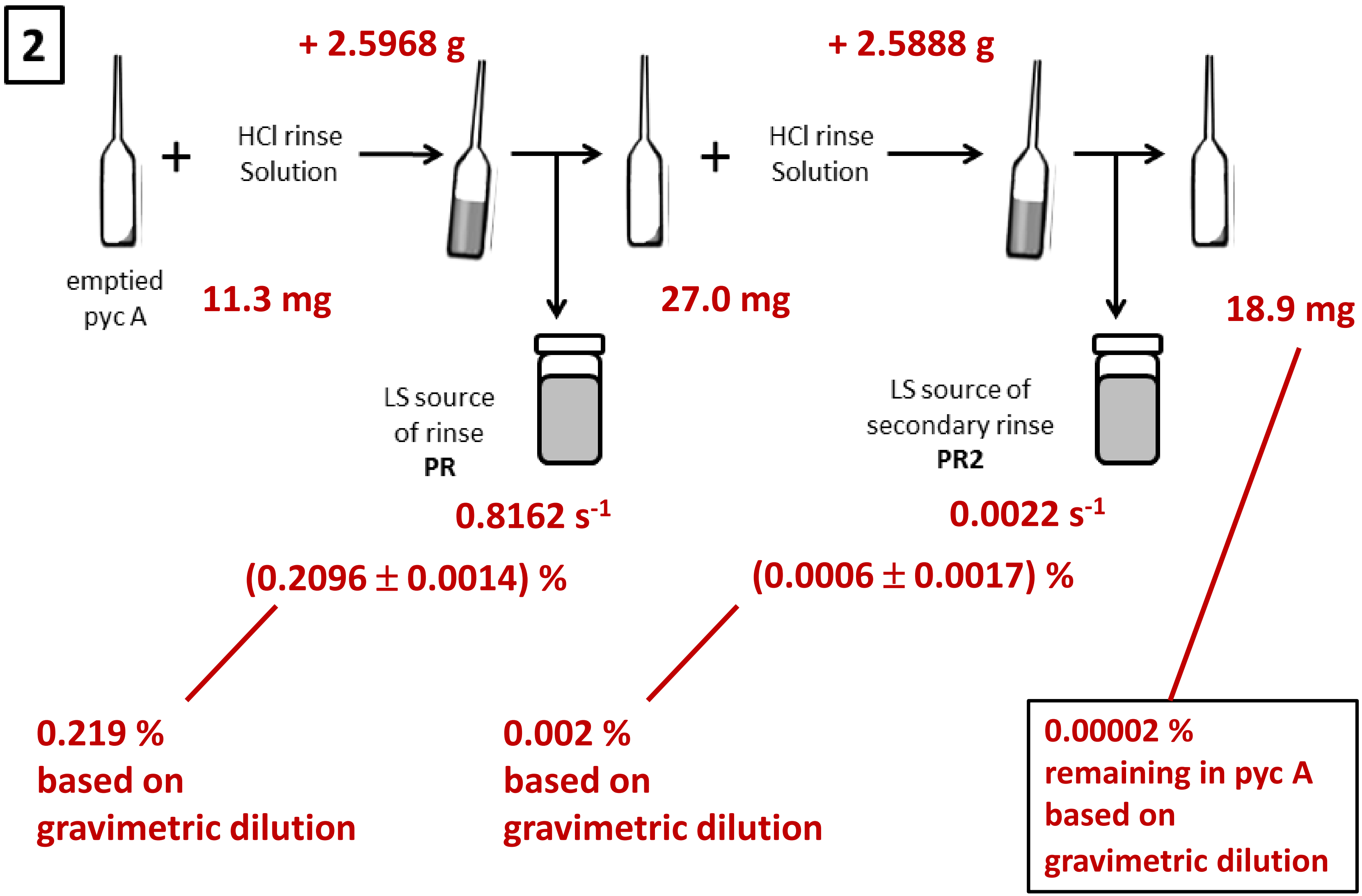


53 mg solution after rinses

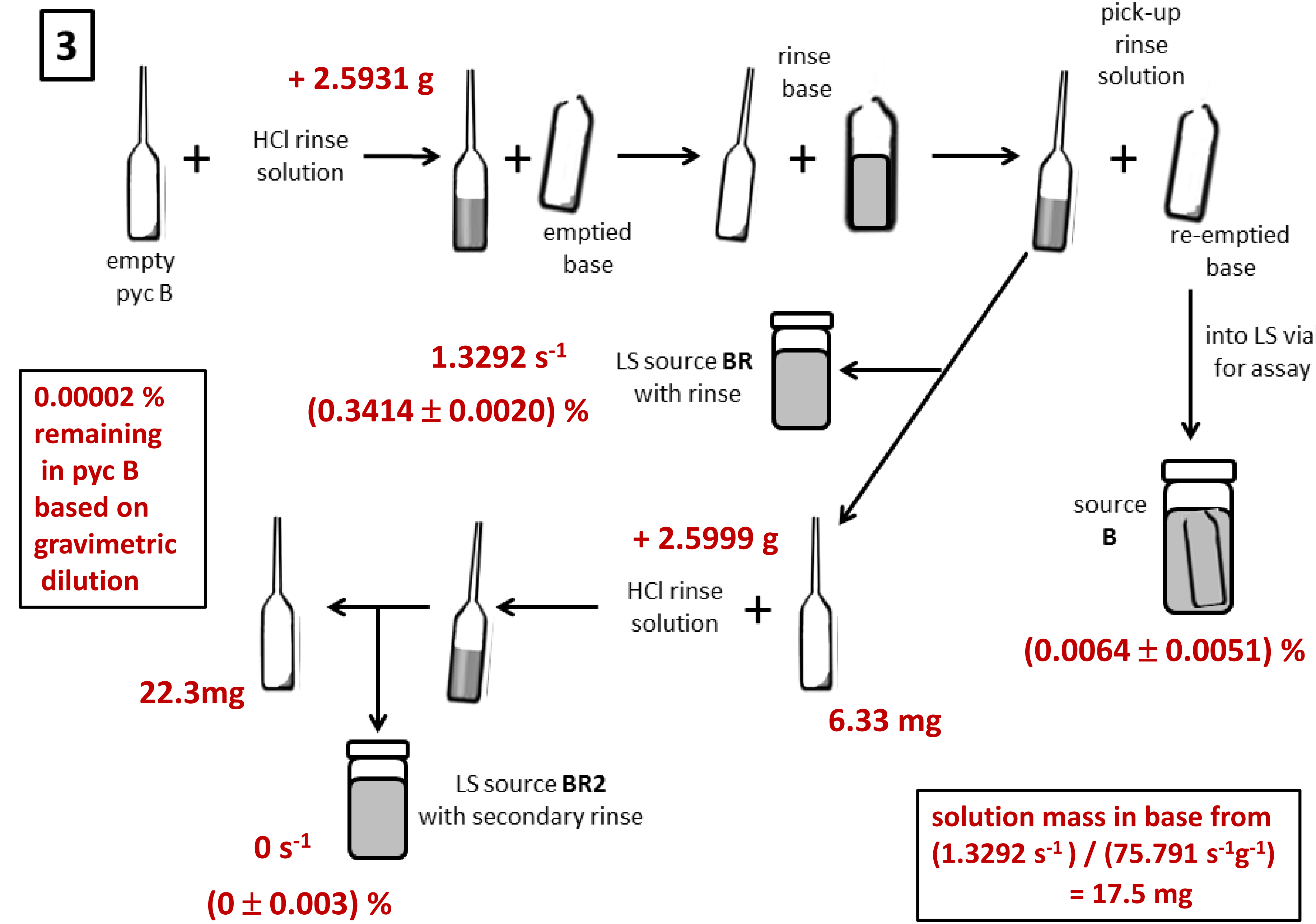
(glass 4.1441 g from pieces)

75.791 $s^{-1}g^{-1}$
S = 0.16 %

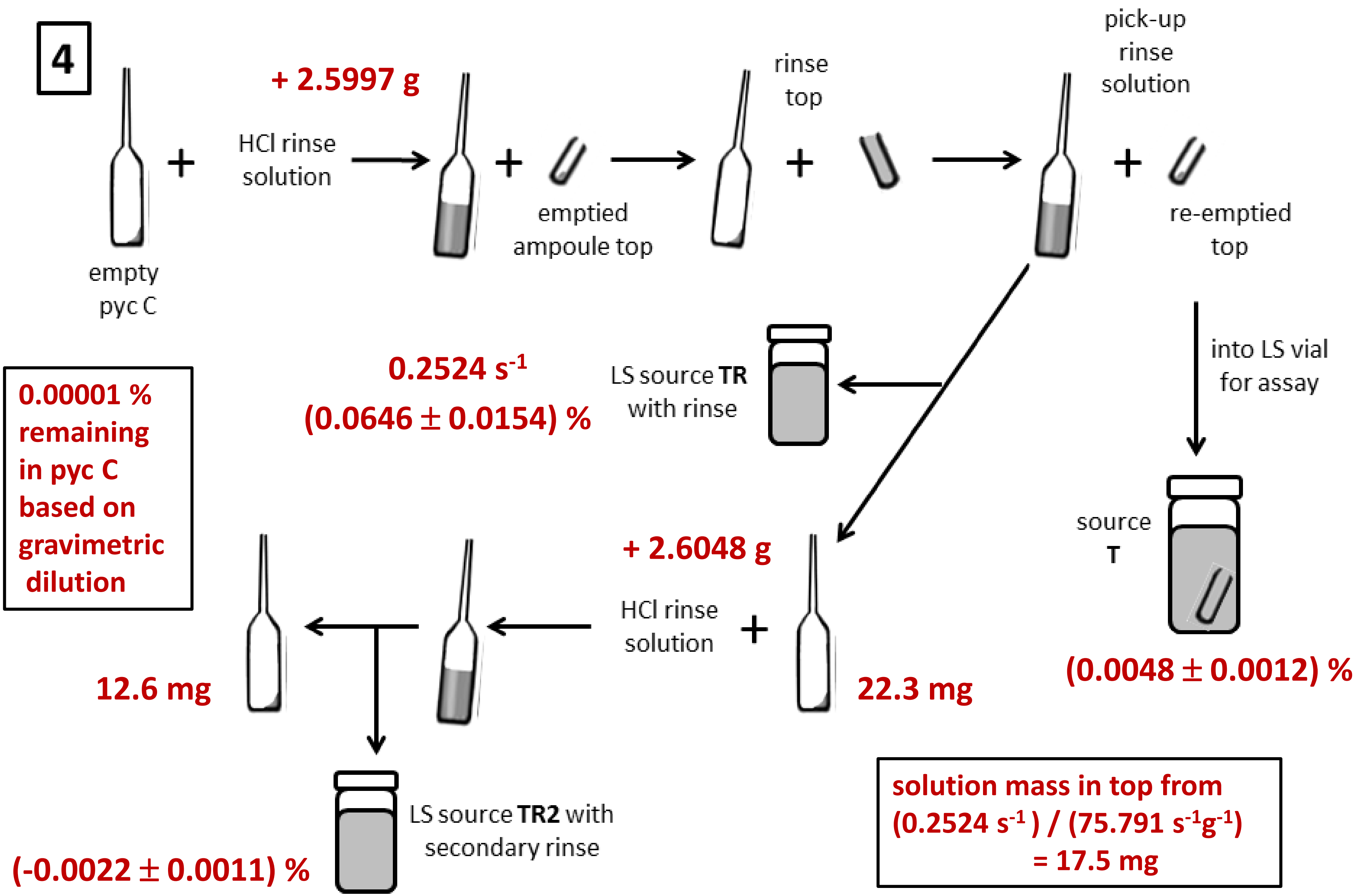
rinse transfer pycnometer



rinse ampoule base



rinse ampoule top



	PR	PR2	BR	BR2	TR	TR2	Base	Top
1	(1.340 ± 0.006) %	***	(1.0805 ± 0.006) %	***	(0.360 ± 0.005) %	***	(0.055 ± 0.003) %	(0.056 ± 0.002) %
2	(0.497 ± 0.007) %	(0.006 ± 0.003) %	(0.772 ± 0.007) %	(0.024 ± 0.005) %	(0.116 ± 0.005) %	(-0.002 ± 0.002) %	(0.405 ± 0.014) %	(0.098 ± 0.012) %
3	(0.2096 ± 0.0014) %	(0.006 ± 0.017) %	(0.341 ± 0.002) %	(0 ± 0.003) %	(0.065 ± 0.015) %	(-0.002 ± 0.001) %	(0.006 ± 0.005) %	(0.0048 ± 0.0012) %
4	0.770 ± 0.003) %	0.0098 ± 0.0031) %	0.941 ± 0.004) %	0.0011 ± 0.0028) %	0.172 ± 0.005) %	0.004 ± 0.003) %	0.009 ± 0.012) %	(0.012 ± 0.006) %

Percent of total activity in ampoule

EXPT	1 (2013)	2 (2005)	3 (1993)	4 (1994)
age	1.82 a	9.88 a	22.42 a	21.67 a
solution mass	1.81 g	3.09 g	5.14 g	2.70 g
In glass	0.111 ± 0.005	0.503 ± 0.026	0.011 ± 0.006	0.021 ± 0.021
In rinses	2.780 ± 0.010	1.413 ± 0.013	0.617 ± 0.023	1.898 ± 0.009
	different procedure	**dirty ampoule**	**original ampoule**	

2015 assay results in consideration of 2013 half-life determination

Each grand mean from the 4 expts based on 3 sources each measured for 3 cycles on Beckman LS counter; uncertainty *S* on grand mean for each trial includes within- and between-source variance

T / a	ΔT / d	grand mean E_α / (s^{-1} g^{-1})	S / %	U / %	n
2015.71657	1.119	75.773	0.20	0.25	3
2015.74152	3.228	75.903	0.17	0.23	3
2015.77882	3.991	75.791	0.16	0.22	3
2015.82904	3.195	75.885	0.09	0.17	3

Great-grand mean E_α = 75.838 s^{-1} g^{-1}
S = 0.16 %
U = 0.22 %
N = 4
T = 2015.77281 a
ΔT = 22.696 d

Compare to previous determinations using half-life = 125.2 a (Collé et al., 2014)

N.B. two 193 values were combined as in half-life paper

T / a	*ΔT* / d	great-grand mean E_α / (s^{-1} g^{-1})	*S* / %	*U* / %	*n*	*decay time / a*	E_α at 2015	*% diff from 2015* E_α
1993.31445	86.848	85.913	0.20	0.23	12	22.45837	75.868	+ 0.040
1994.18493	7.521	85.434	0.12	0.19	4	21.58788	75.810	- 0.037
2005.86486	3.172	80.210	0.10	0.14	4	9.90795	75.929	+ 0.119
2013.92065	9.316	76.526	0.23	0.34	8	1.85216	75.745	- 0.122
2015.77281	22.696	75.883	0.16	0.22	4	0		

Ergo, half-life is correct

and solution is stable to sampling over 22.5 years

2013 half-life determination

with n = 4 values (combining two 1993 results)

unwgt'd fit = 124.4 a

U wgt'd fit = (126.0 ± 2.5) a

ave U wgt'd fit = (124.4 ± 2.1) a

(125.2 ± 3.3) a

fit = 2.3 a

wgt model = 0.3 a

warping = 2.4 a

0.24 %

1.0 %

***n* = 4 + "2015"**

unwgt'd fit = 124.7 a

U wgt'd fit = (124.7 ± 1.3) a

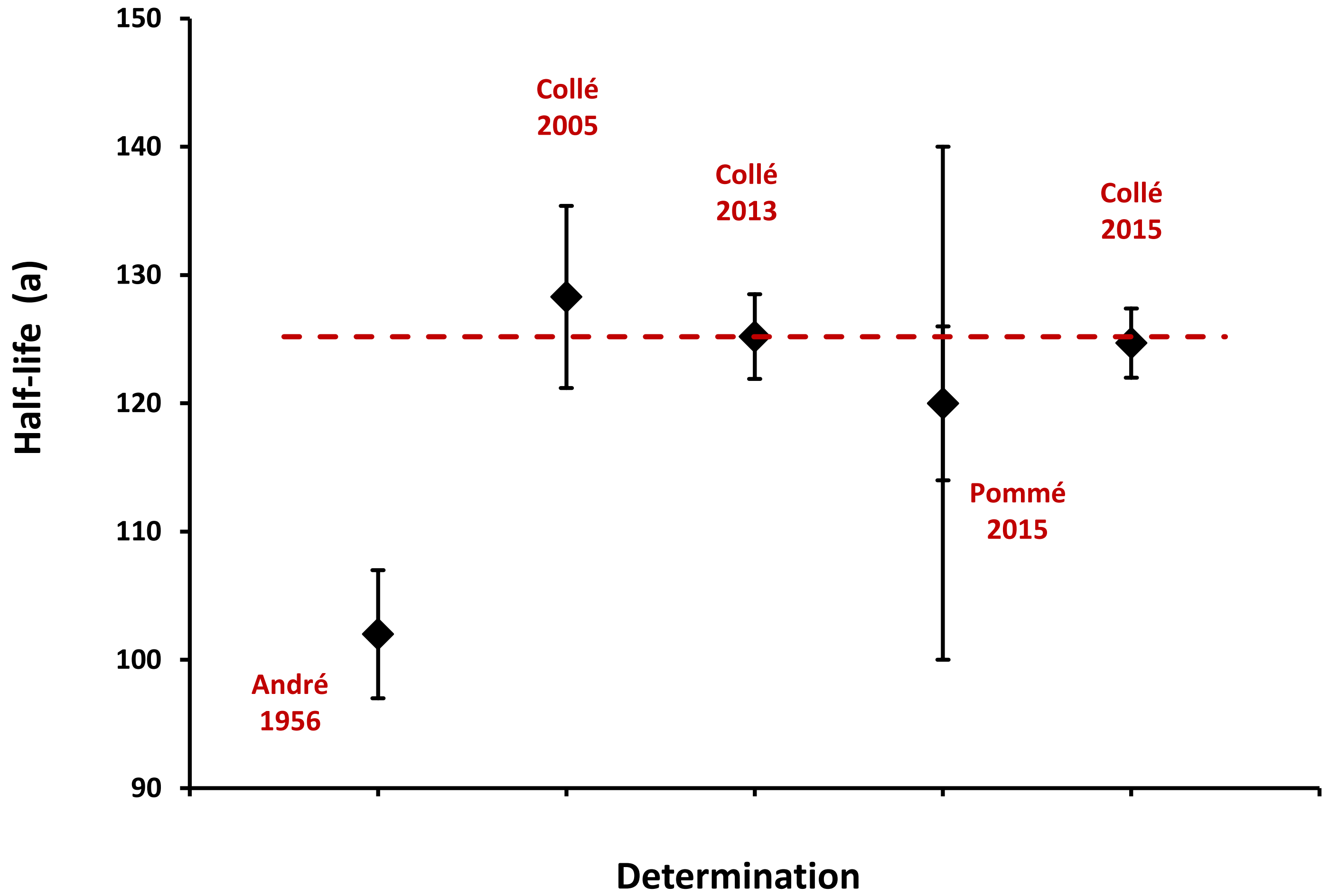
fit uncertainties are 68 % CL

Fitzgerald, private communication (2015)

".. change in value is about 20 % of the original uncertainty in the fit, or about 30 % of the new uncertainty in the fit ... and 10 % of the total uncertainty reported in the paper" (since we included the warping uncertainty)

"... validates our choice of 'delta' for the warping uncertainty as being not too small to account for any solution instabilities" (i.e., long-term effects)

GLORY


Half-life (a)
150
140
130
120
110
100
90
Collé
2005
Collé
2013
Collé
2015
Pommé
2015
André
1956
Determination

CREDITS

Thanks for loan of the balance

You can get it back now – but I'd prefer NOT ! ! !

CREDIT MEMES