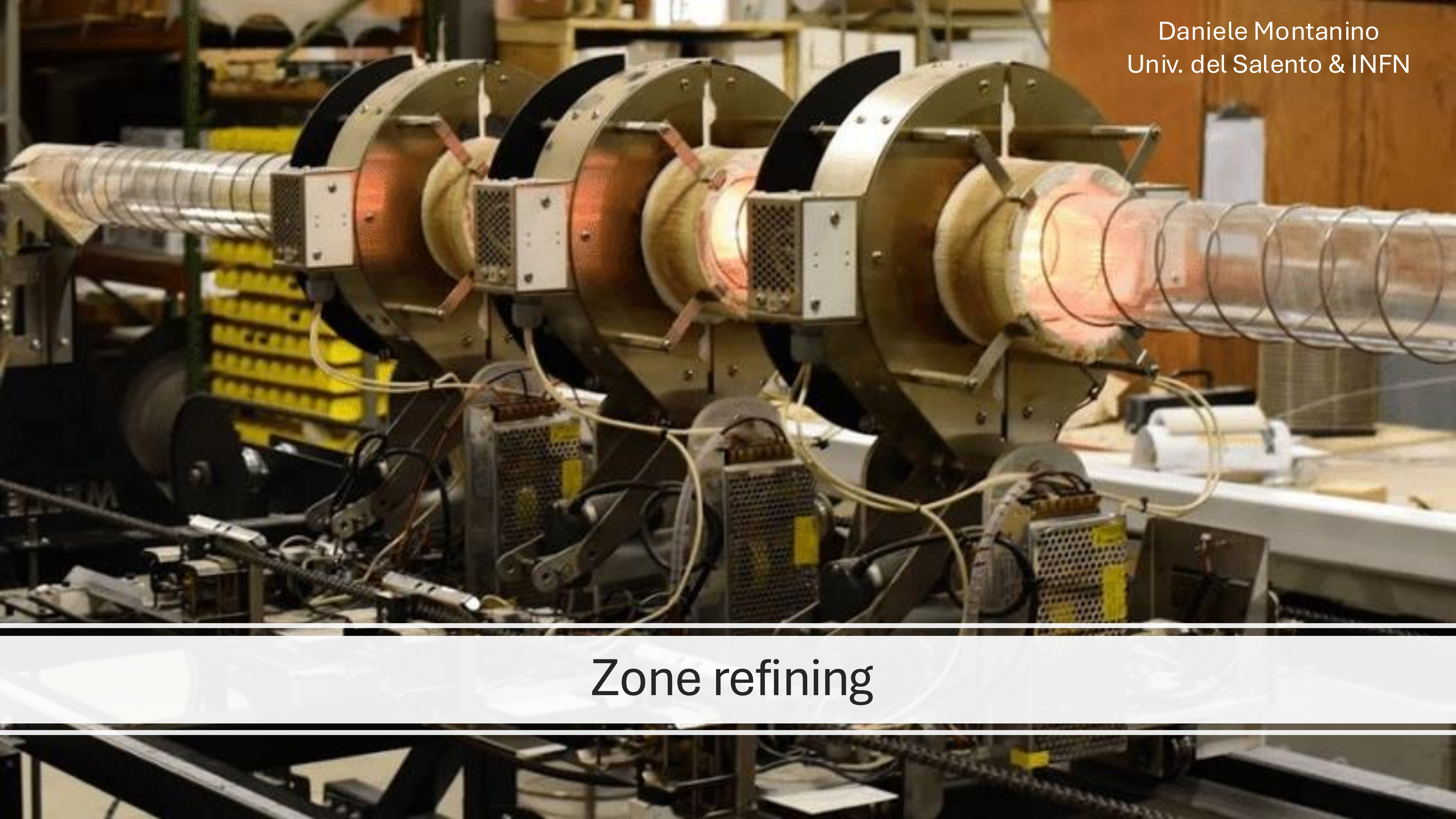
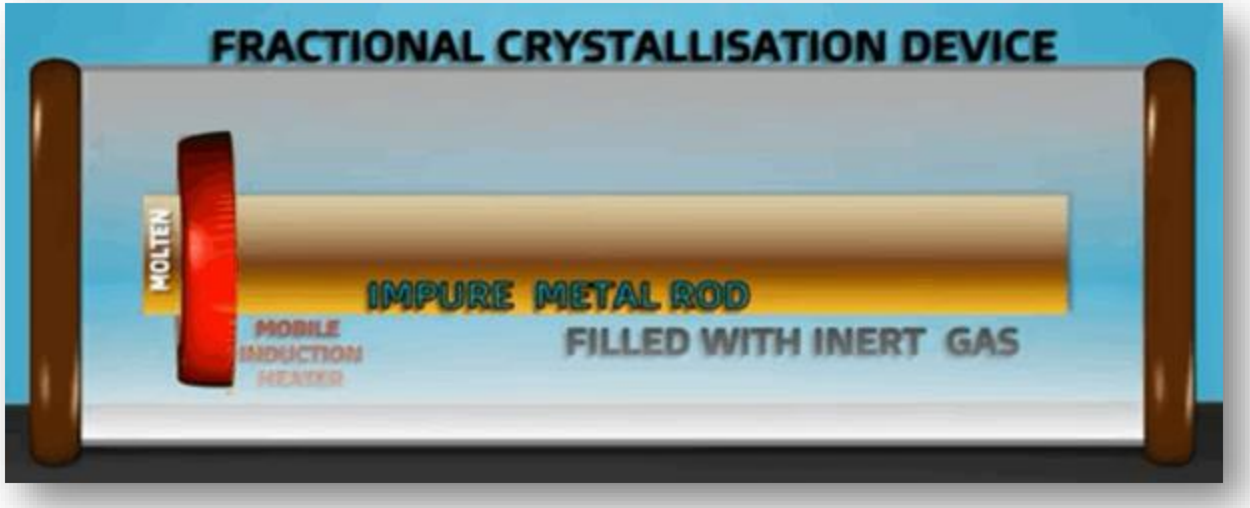
Daniele Montanino
Univ. del Salento & INFN

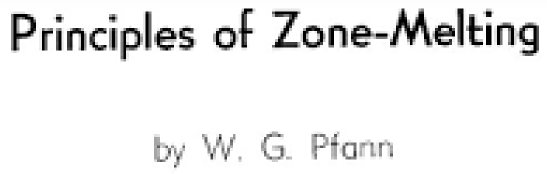


Zone refining

Zone refining

- Zone refining (or zone melting) was invented in the Early 50’s by J.D. Bernal and developed by W.G. Pfann in Bells Laboratories to prepare high-purity materials (mainly semiconductors)
- A narrow region of a crystal is melted, and this molten zone is moved through the crystal. The molten region melts impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the ingot.

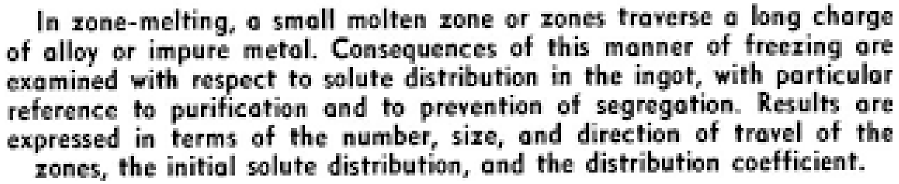




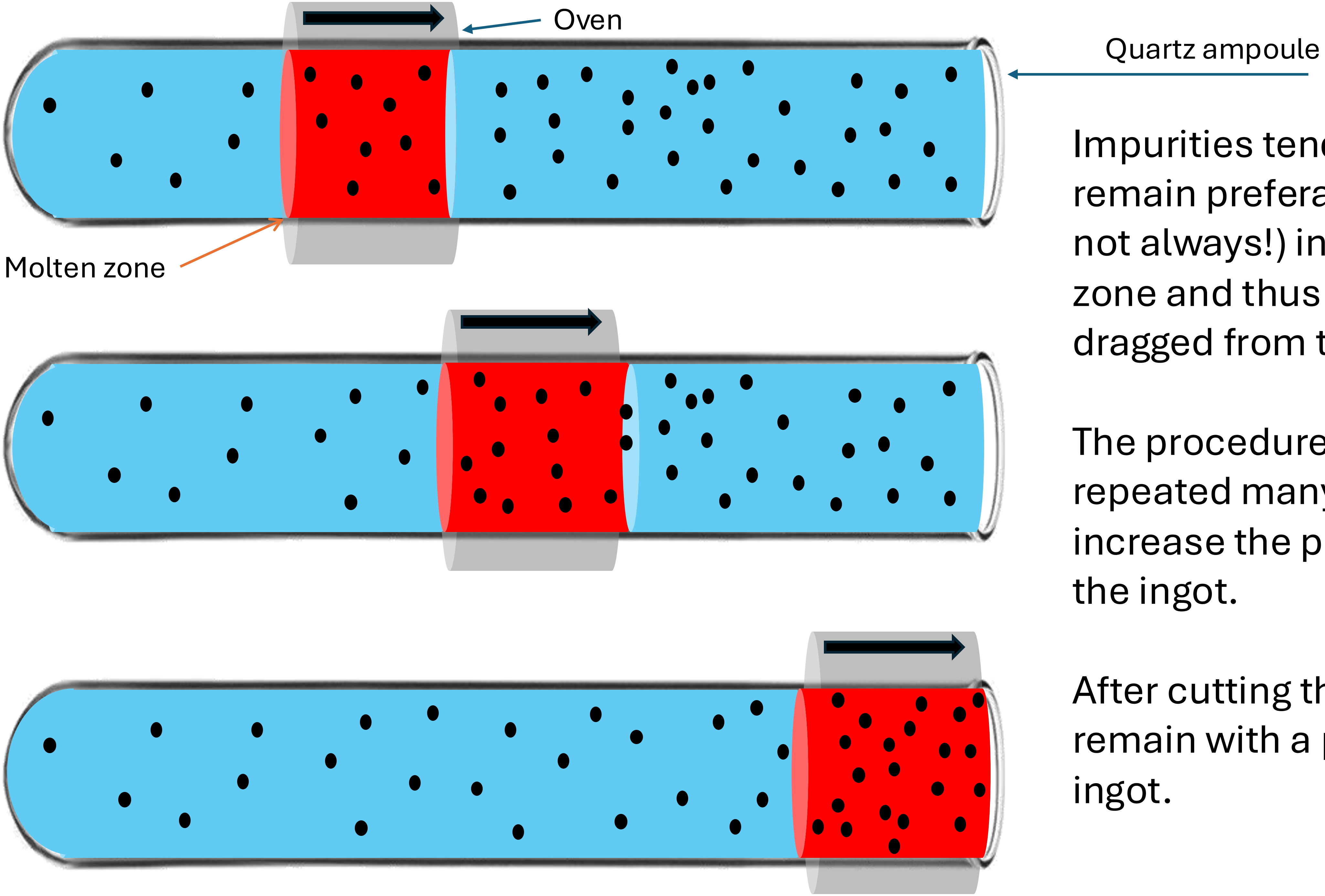
Principles of Zone-Melting

by W. G. Pfann

The Journal of The Minerals, Metals & Materials Society 4, 747 (1952)



In zone-melting, a small molten zone or zones traverse a long charge of alloy or impure metal. Consequences of this manner of freezing are examined with respect to solute distribution in the ingot, with particular reference to purification and to prevention of segregation. Results are expressed in terms of the number, size, and direction of travel of the zones, the initial solute distribution, and the distribution coefficient.



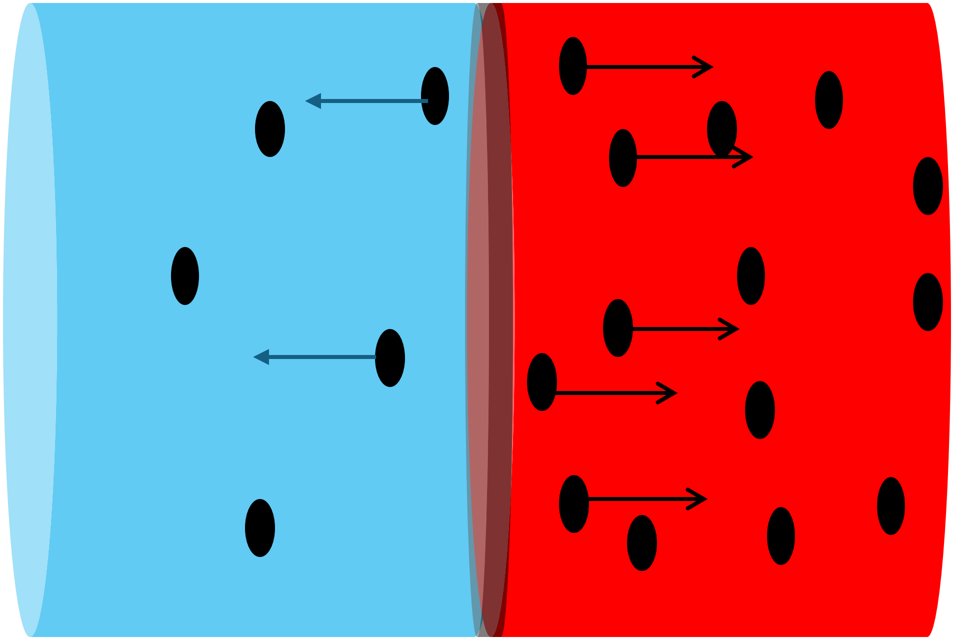
Impurities tend to remain preferably (but not always!) in the liquid zone and thus are dragged from tip to tail.

The procedure can be repeated many times to increase the purity of the ingot.

After cutting the tail we remain with a purified ingot.

After solidification in the interface between liquid and solid a fraction k (*coefficient of segregation*) of impurities contained in the liquid remain in the solid

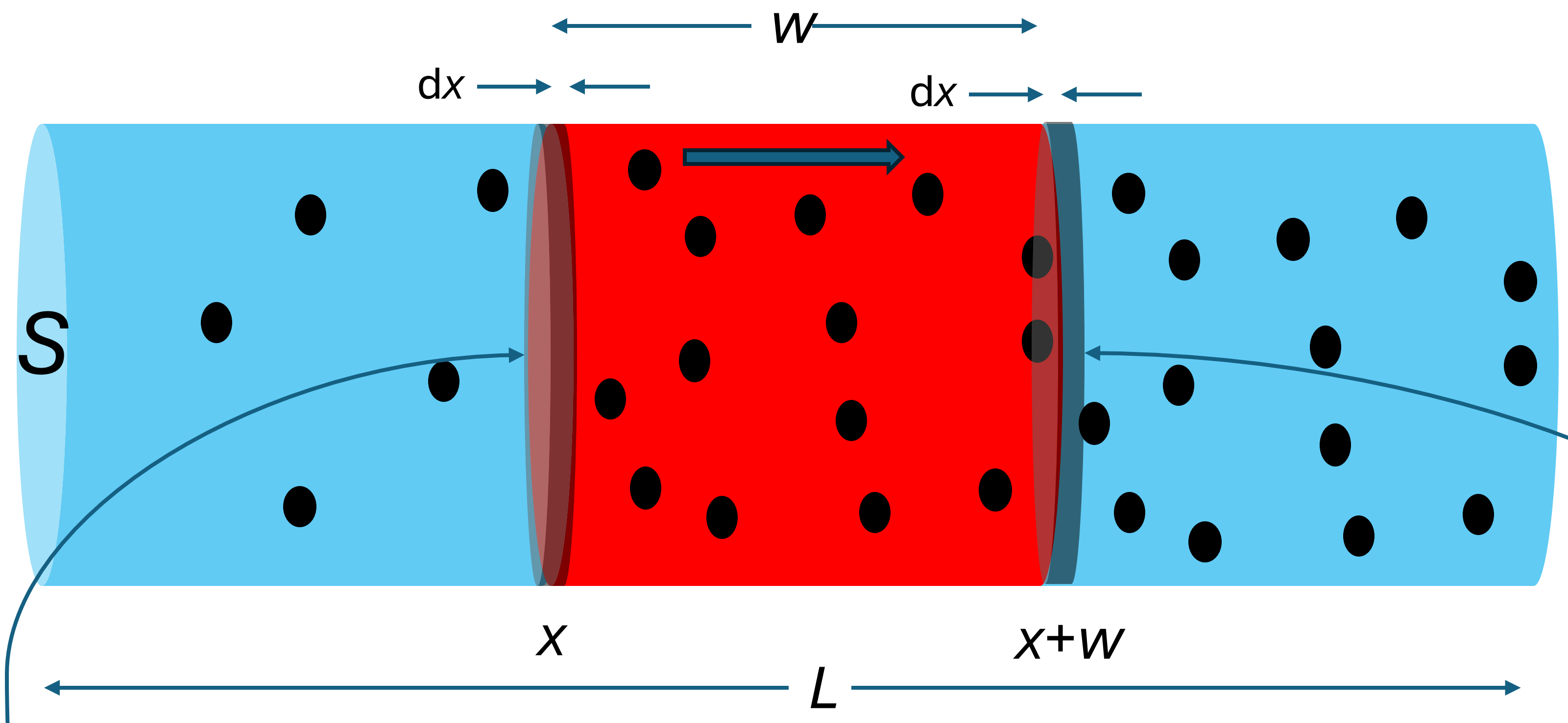
$$C_S = kC_L$$



where C_s (C_L) is the concentration of pollutant per volume unit in the solid (liquid).

If $k<1$ ($k>1$) the pollutant remains preferably in the molten (frozen) zone.

Theory of zone refining



$$wSdC_L = -C_s(x)Sdx + C_s(x+w)Sdx$$

Variation of solute in the molten zone

Solute entering in the freezing zone

Solute entering in the molten zone

Remembering that at point *x* the variation of the solute entering in the freezing zone is

$$dC_S(x) = k\,dC_L(x)$$

and thus

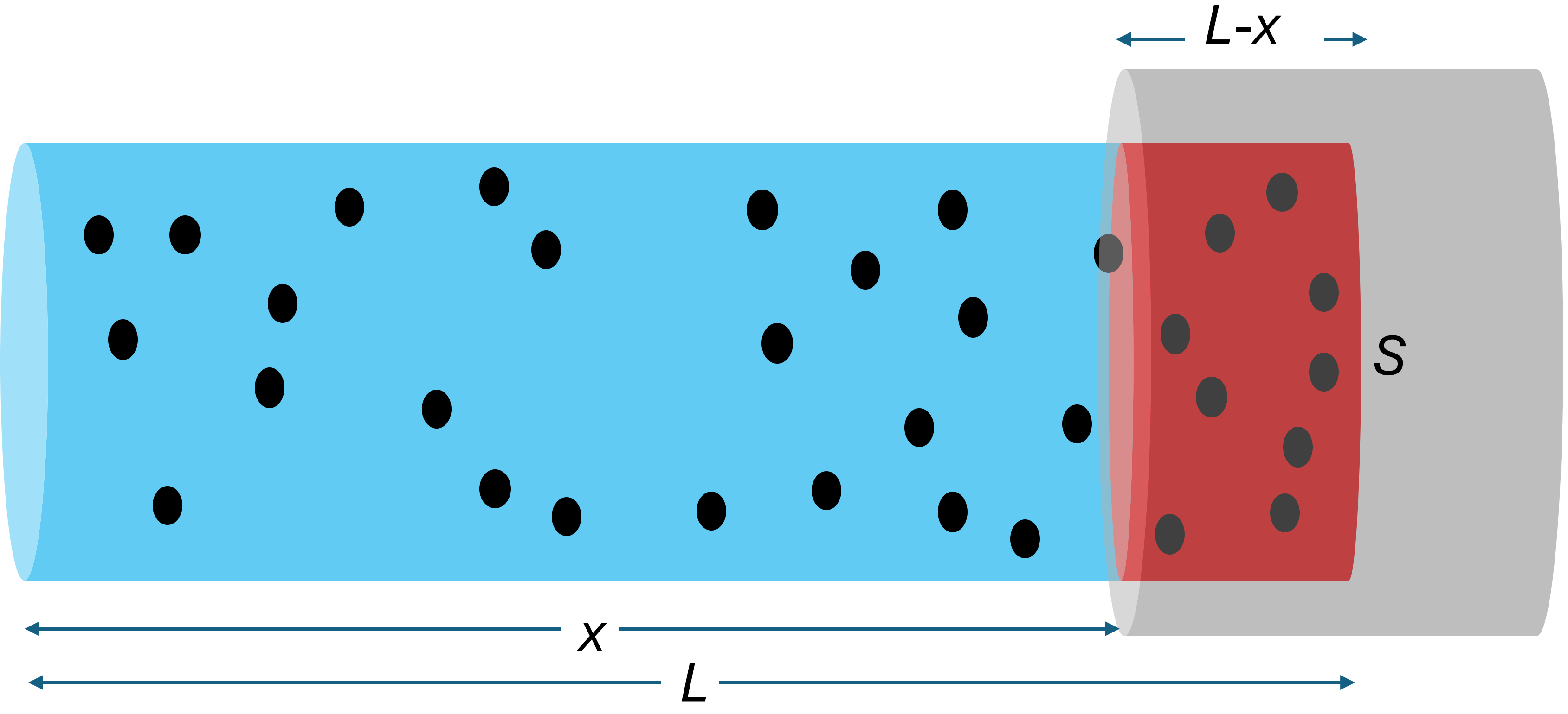
$$\frac{dC_{S,\mathrm{after}}(x)}{dx} = \frac{k}{w}\left[C_{S,\mathrm{before}}(x+w) - C_{S,\mathrm{after}}(x)\right]$$

Previous equation is valid only if the pollutant diffuses uniformly in the molten zone. The effective segregation coefficient in the process is given by

$$k_{\mathrm{eff}} = \frac{k}{k + (1-k)\exp\left(-\frac{V\delta}{D}\right)}$$

with V=moving rate of the oven, D=diffusion coefficient, δ=thickness of the diffusion boundary layer (fraction of mm). Diffusion coefficient in molten salts is usually O(10^{-5} cm^2/s). If $V<D/\delta \sim$ mm/h we have $k_{\mathrm{eff}} \rightarrow k$. Convection due to temperature gradient and Marangoni convection can contribute to diffusion.

Tail zone: when the oven reaches and overcomes the end of ingot, the equation is different

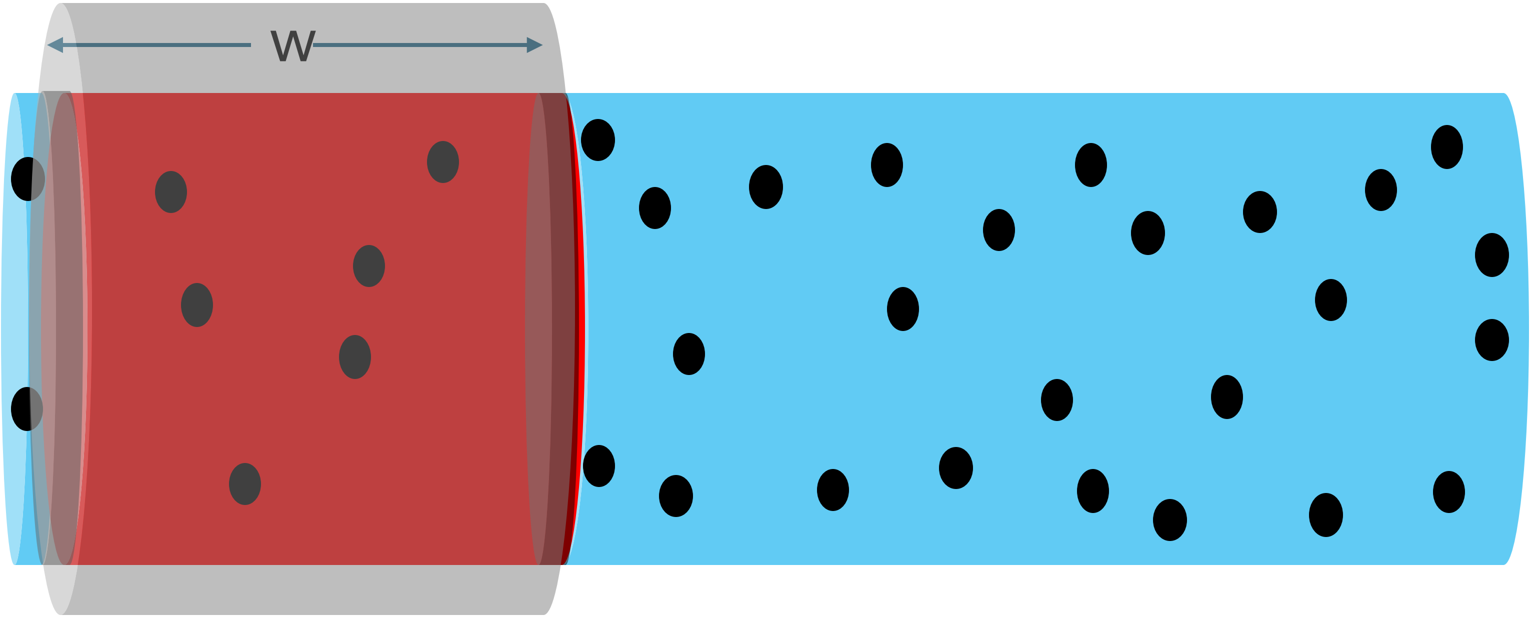


$$Sd[(L-x)C_L] = -C_s(x)Sdx$$

Variation of solute in the molten zone = solute entering in the freezing zone

$$\frac{dC_S(x)}{dx} = \frac{1-k}{L-x}C_S(x) \longrightarrow C_S(x) = C_S(L-w)\left(\frac{L-x}{w}\right)^{k-1}$$

<u>Starting condition</u>: in the tip enters a fraction k of the average concentration of the molten zone



$$C_{S,\mathrm{after}}(0) = k\overline{C_{S,\mathrm{before}}} = \frac{k}{w}\int_0^w C_{S,\mathrm{before}}(x)dx$$

Recap: suppose to repeat the procedure *n* times. The equations to solve are

$$C_n'(x) = \frac{k}{w}\left[C_{n-1}(x+w) - C_n(x)\right] \quad \text{if} \quad x \le L - w$$

$$C_n(x) = C_n(L-w)\left(\frac{L-x}{w}\right)^{k-1} \quad \text{if } L - w < x \le L$$

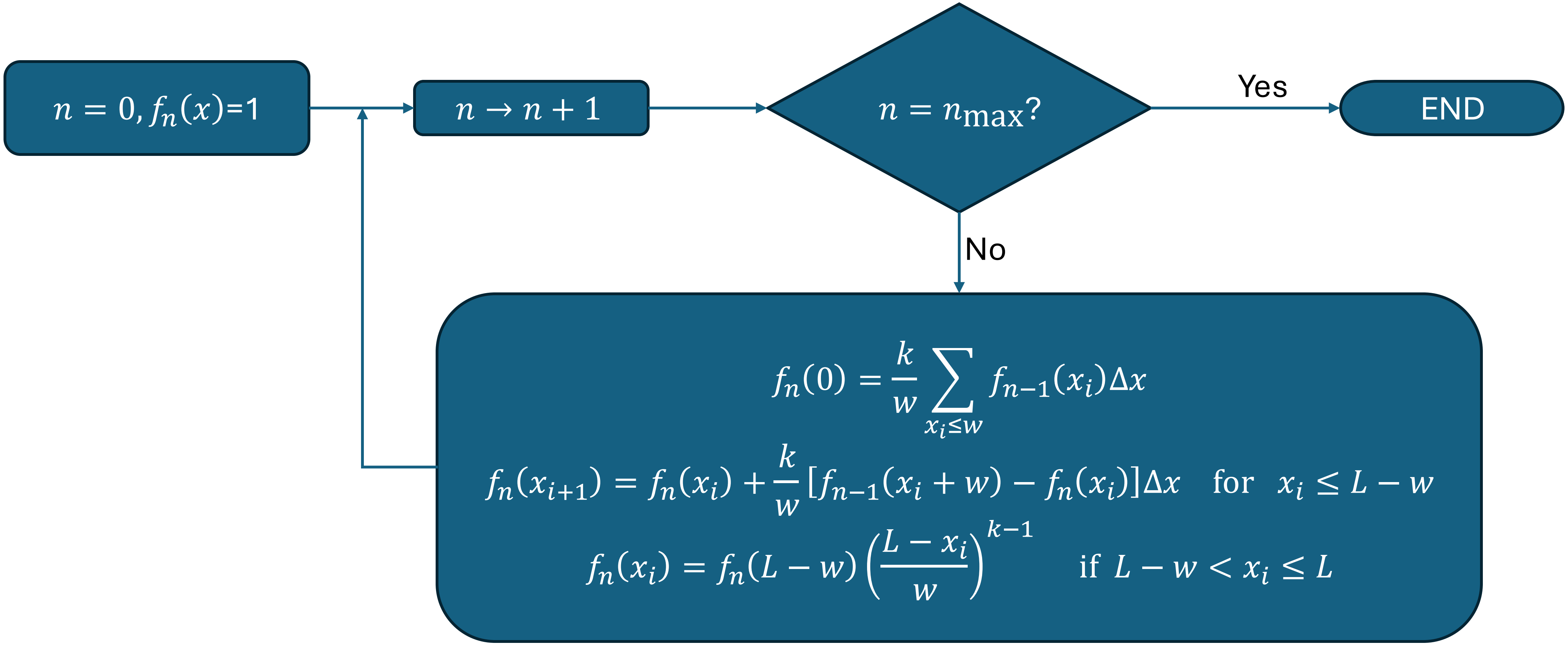
$$C_n(0) = \frac{k}{w}\int_0^w C_{n-1}(x)dx$$

We suppose that initially the ingot has a constant concentration $C_0(x)=C_0$.
The functions $f_n(x)=C_n(x)/C_0$ follow the previous equations but with $f_0=1$.

For f_1(x) we have a simple analytic solution

$$f_1(x) = 1 - (1-k)e^{-\frac{kx}{w}} \qquad \text{if} \qquad x \le L - w$$

Anyway, for *n*>1 the equations must be solved through a numerical iterative procedure



$n = 0, f_n(x)$=1

$n \to n + 1$

$n = n_{\max}?$

Yes

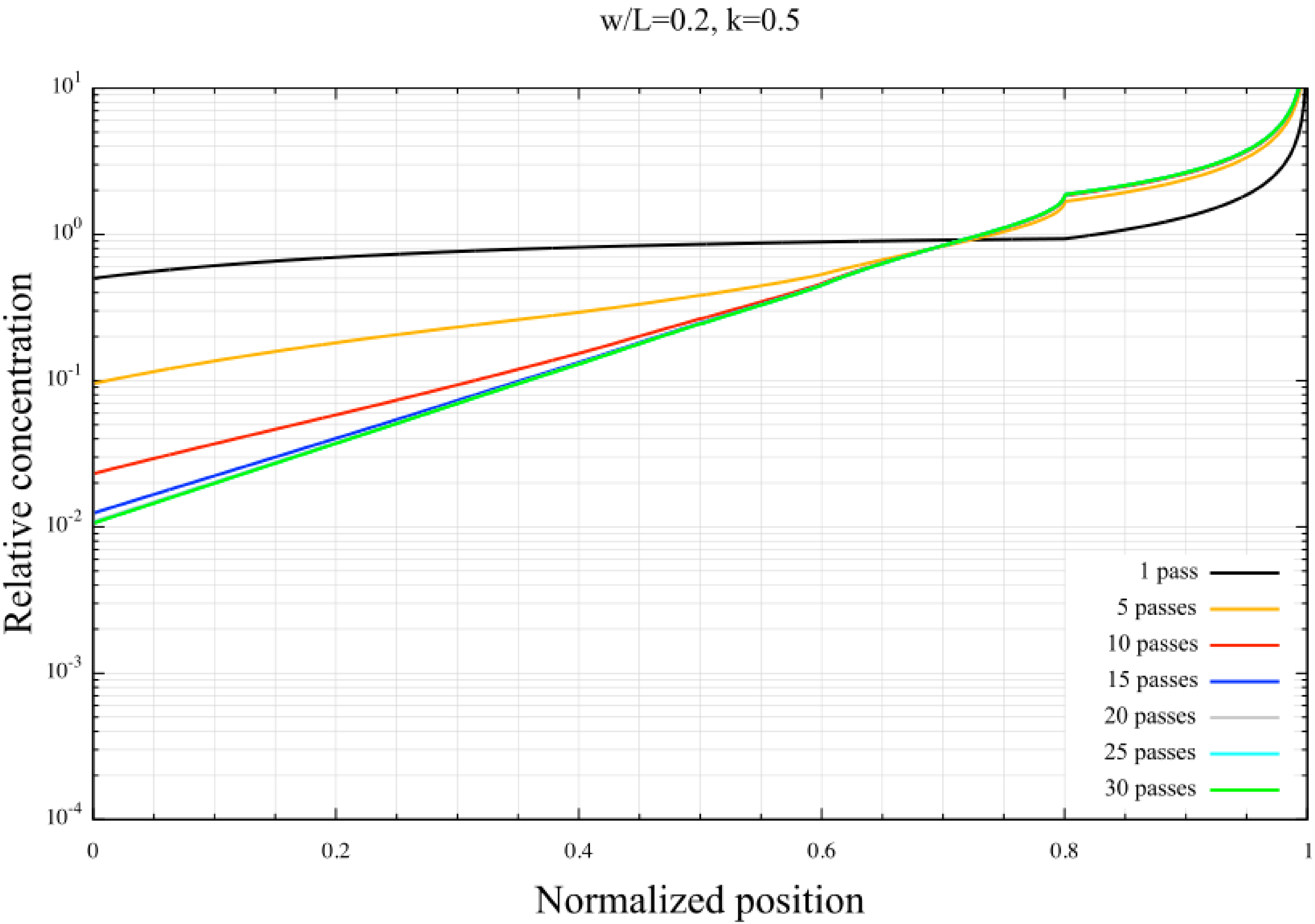
END

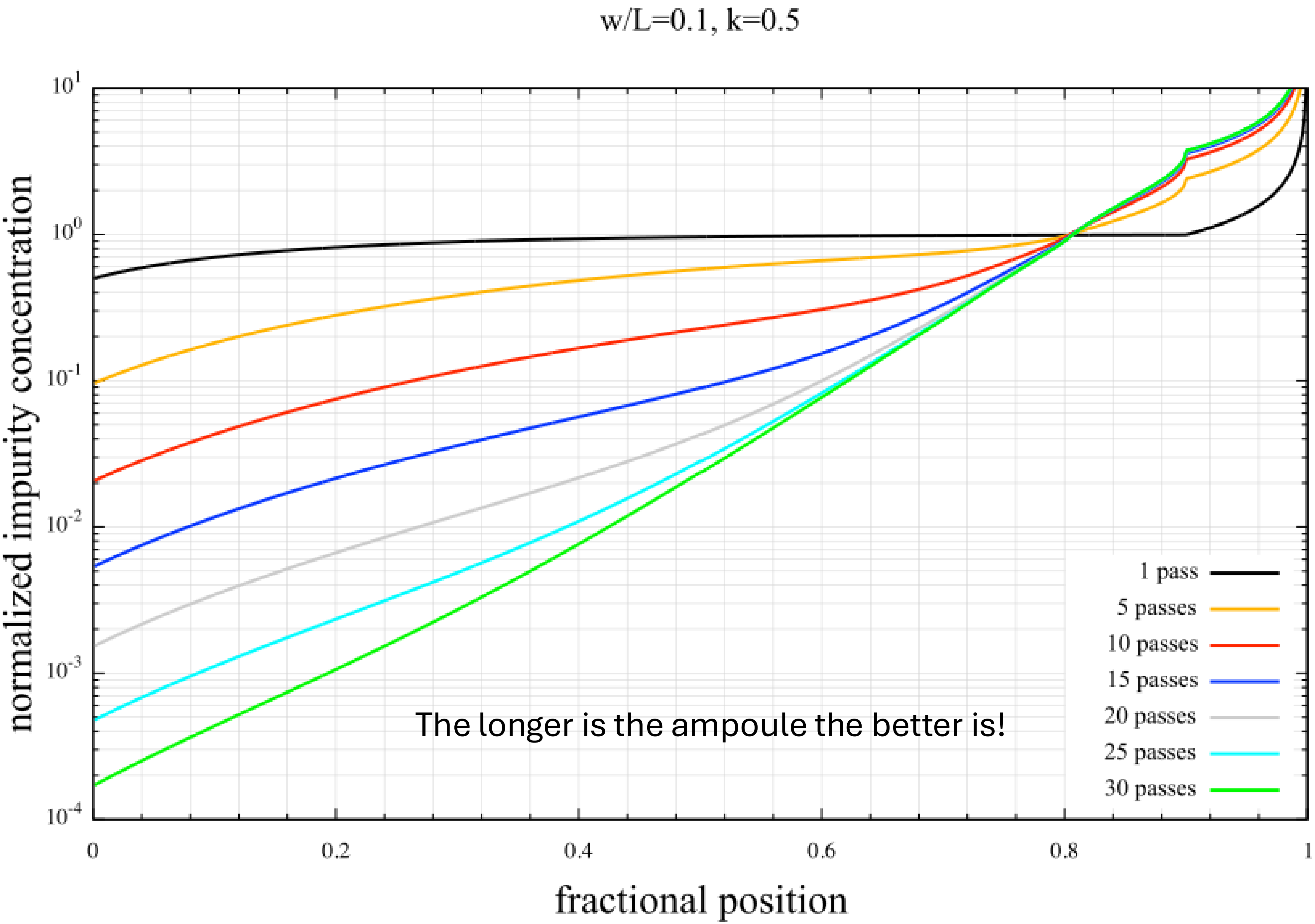
No

$$f_n(0) = \frac{k}{w} \sum_{x_i \le w} f_{n-1}(x_i)\Delta x$$

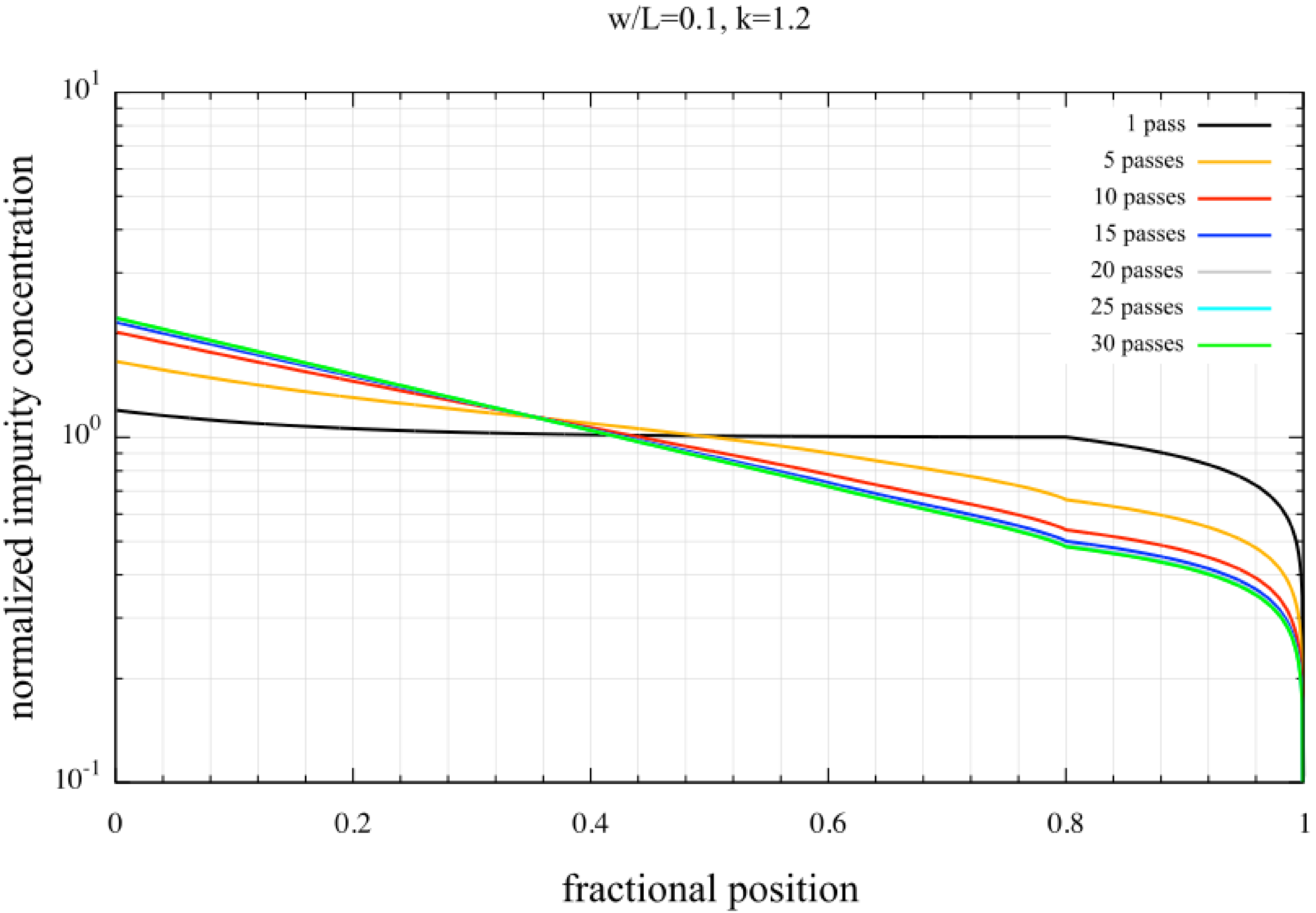
$$f_n(x_{i+1}) = f_n(x_i) + \frac{k}{w}\left[f_{n-1}(x_i + w) - f_n(x_i)\right]\Delta x \quad \text{for} \quad x_i \le L - w$$

$$f_n(x_i) = f_n(L-w)\left(\frac{L - x_i}{w}\right)^{k-1} \qquad \text{if} \;\; L - w < x_i \le L$$


w/L=0.2, k=0.5
Relative concentration
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0
0.2
0.4
0.6
0.8
1
Normalized position
1 pass
5 passes
10 passes
15 passes
20 passes
25 passes
30 passes



The longer is the ampoule the better is!


w/L=0.1, k=1.2
1 pass
5 passes
10 passes
15 passes
20 passes
25 passes
30 passes
10^1
10^0
10^{-1}
normalized impurity concentration
0
0.2
0.4
0.6
0.8
1
fractional position

Limit ("ultimate") solution: repeating the procedure to infinity is useless. In fact, for increasing n a limiting solution is reached. For n→∞ the equation become

$$f'_\infty(x) = \frac{k}{w}\left[f_\infty(x+w) - f_\infty(x)\right]$$

this equation can be solved by an exponential

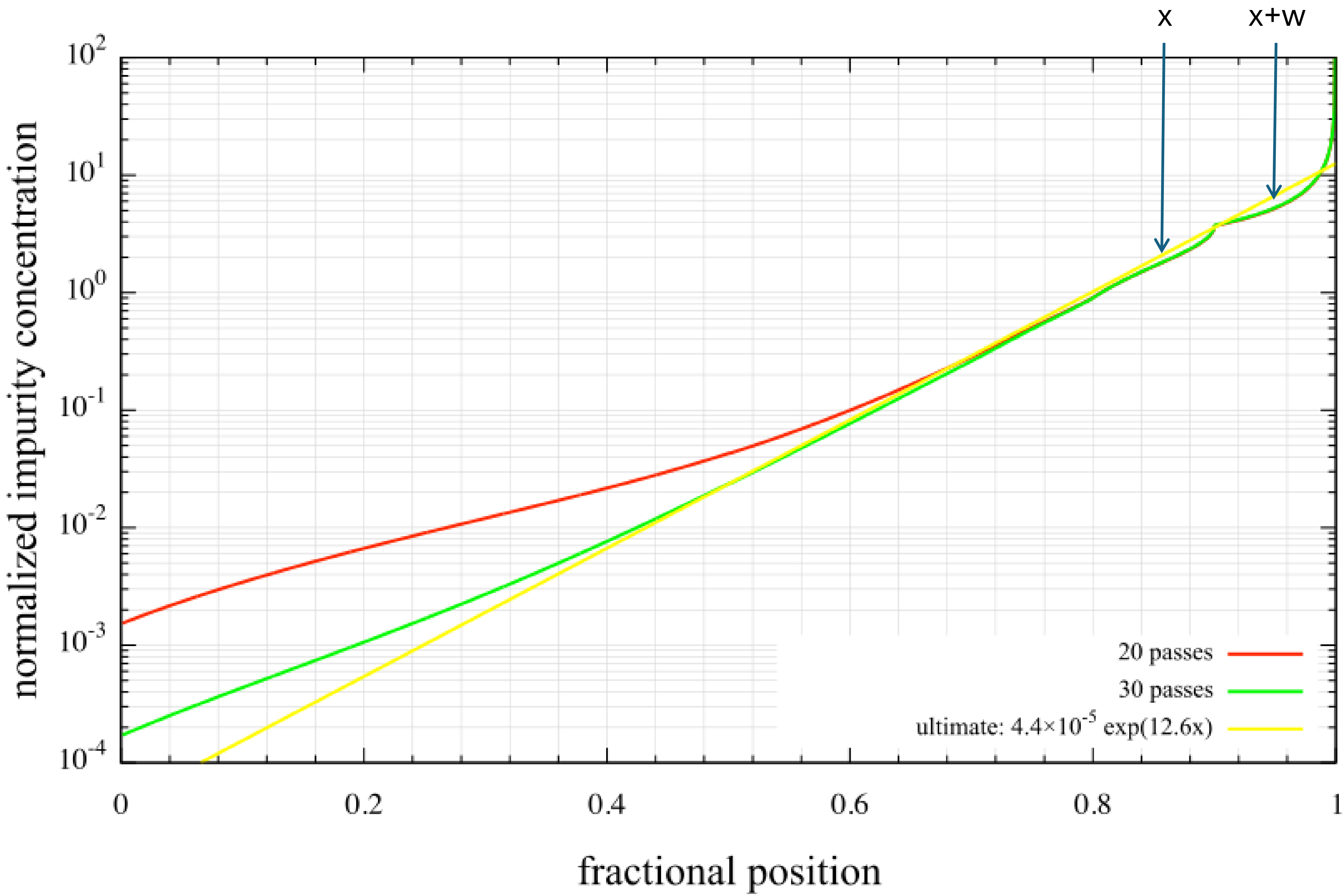
$$f_\infty(x) = Ae^{Bx/w}$$

B is the solution of the transcendent equation $B = k(e^B - 1)$ and *A* can be found imposing the conservation of the solute

$$\frac{1}{L}\int_0^L f_\infty(x)dx = 1 \quad \Longrightarrow \quad A = \frac{BL/w}{e^{BL/w} - 1}$$

However, this is only an approximate solution since for x>*L*-*w* the solution is a power-law and not exponential!

w/L=0.1, k=0.5

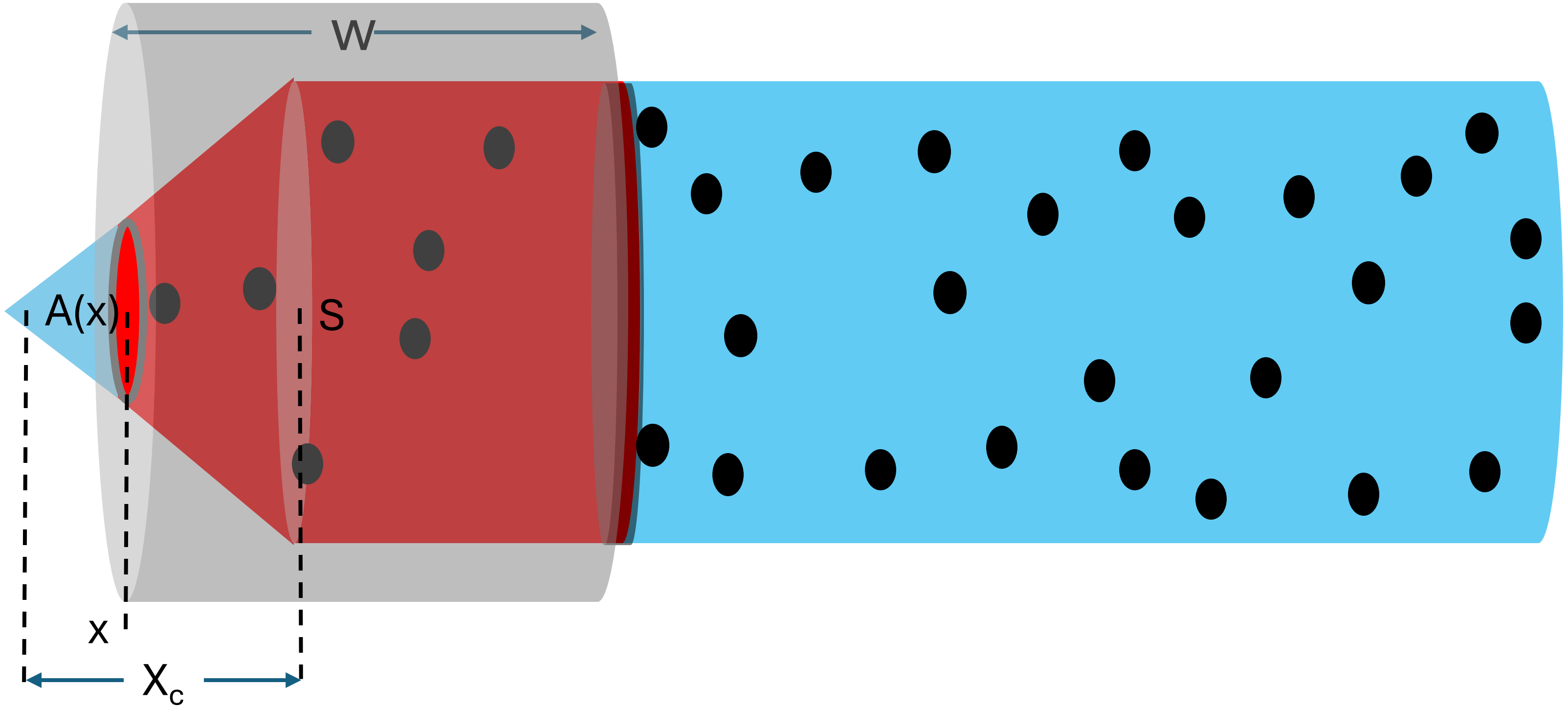


$f_\infty(x+w)$
not an exponential

Geometry of the ampoule: the ampoule has a cone-shaped tip

picture of the ampoule taken at Radiation Monitoring Devices

we must take in account the varying cross section of the ampoule.



If *V*(x) is the volume of the molten zone and *A*(x) the cross section of the ampoule at the left side, the equation become

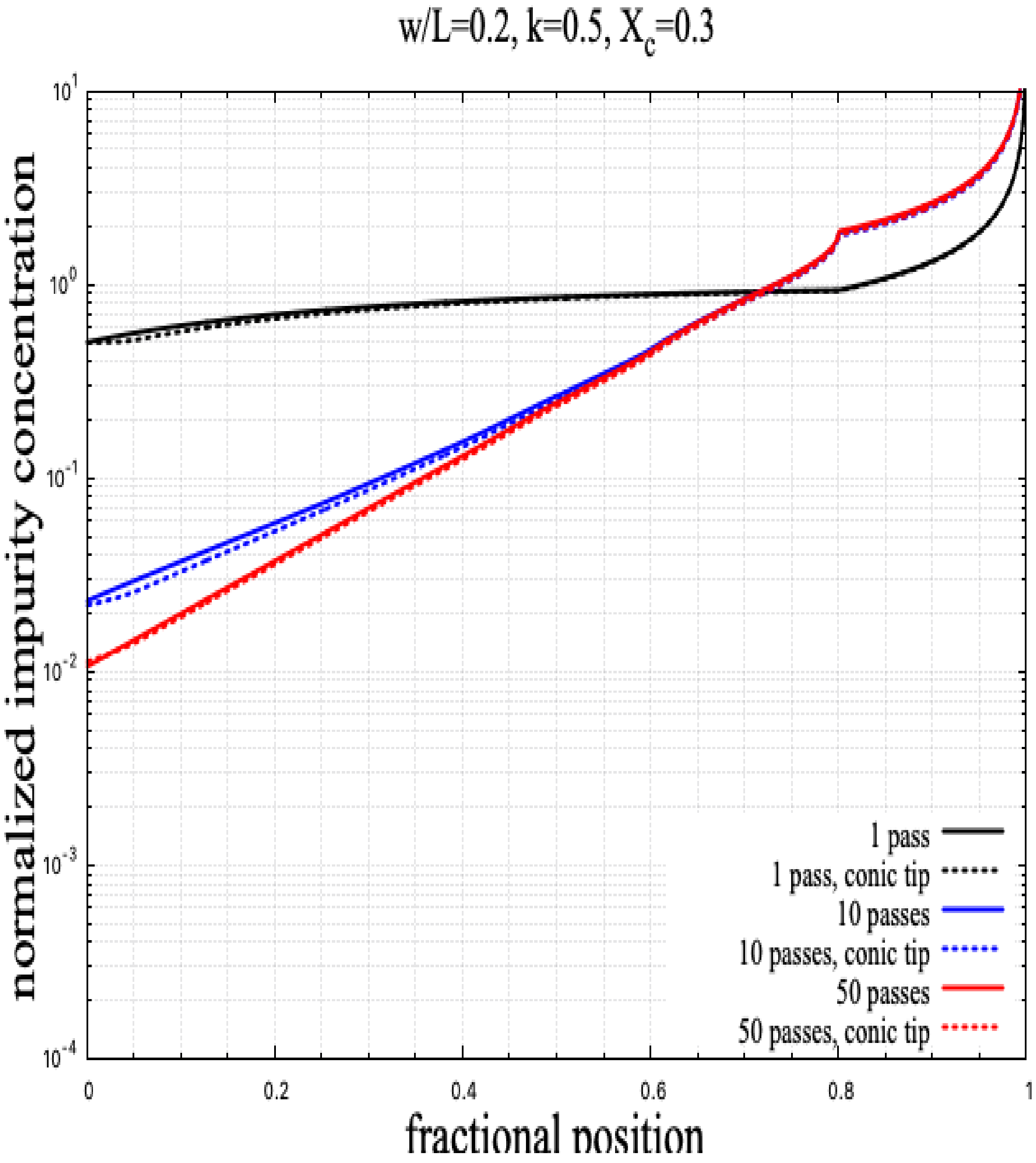
$$d[V(x)C_L] = C_s(x+w)Sdx - C_s(x)A(x)dx$$

After a little algebra we obtain the corrected equation

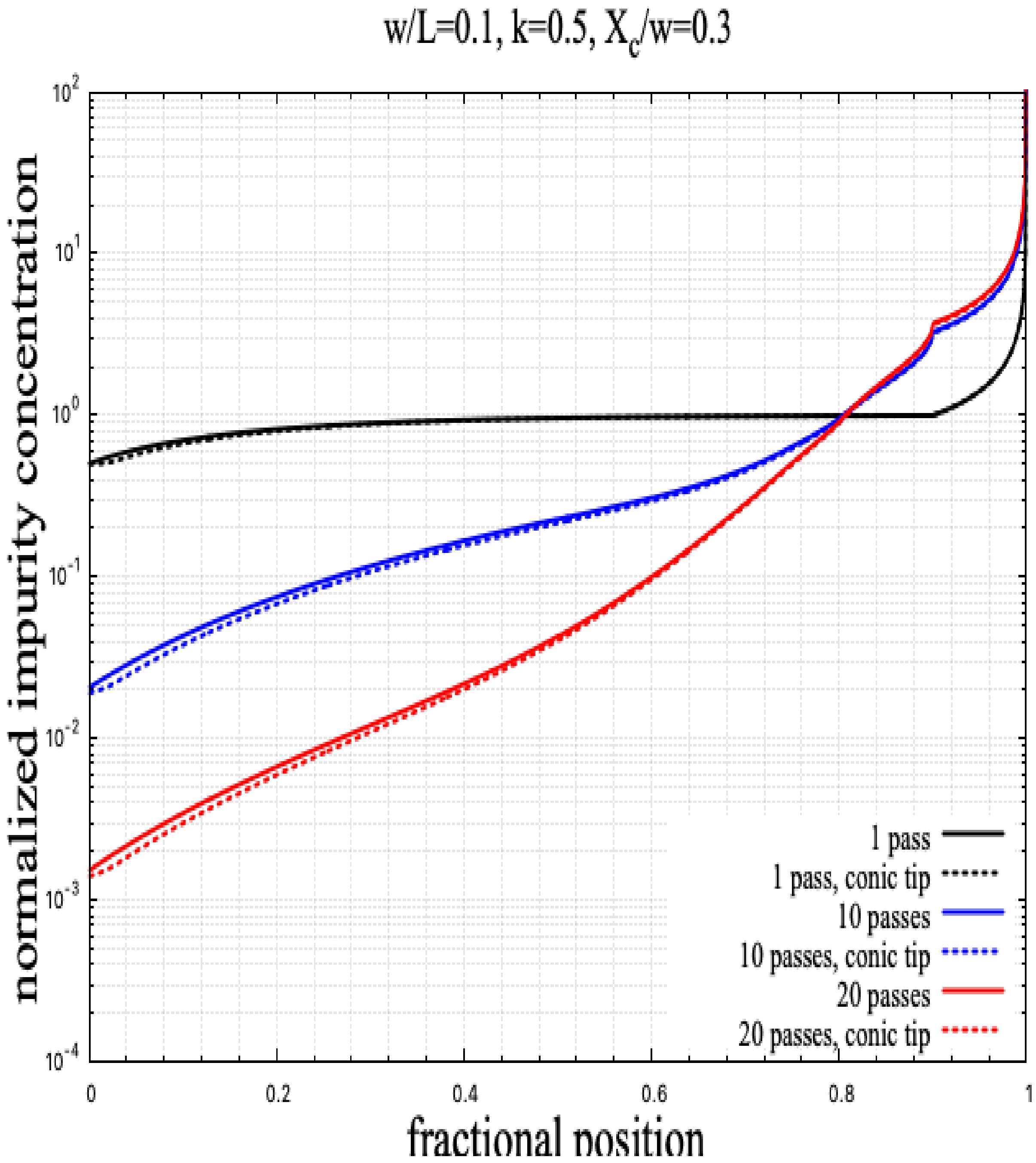
$$C_n'(x) = \frac{S}{V(x)}\left[kC_{n-1}(x+w) - \left(1-(1-k)\frac{A(x)}{S}\right)C_n(x)\right]$$

$$V(x) = S\cdot\begin{cases} w - \frac{2}{3}X_c + x\left(1-\frac{1}{3}\frac{x^2}{X_c^2}\right) & \text{if } x \le X_c \\ w & x > X_c \end{cases}$$

$$A(x) = S\cdot\begin{cases} \frac{x^2}{X_c^2} & \text{if } x \le X_c \\ 1 & x > X_c \end{cases}$$



w/L=0.2, k=0.5, X_c=0.3
normalized impurity concentration
fractional position
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0
0.2
0.4
0.6
0.8
1
1 pass
1 pass, conic tip
10 passes
10 passes, conic tip
50 passes
50 passes, conic tip



w/L=0.1, k=0.5, X_c/w=0.3
normalized impurity concentration
fractional position
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0
0.2
0.4
0.6
0.8
1
1 pass
1 pass, conic tip
10 passes
10 passes, conic tip
20 passes
20 passes, conic tip

Notice that previous equation can be generalized to any geometry of the ampoule. The most general equation is

$$C_n'(x)V(x) = k[C_{n-1}(x+w)A(x+w) - C_n(x)A(x)] - C_n(x)\,[A(x+w) - A(x)]$$

where *A*(*x*) is the cross section of the ampoule at the point *x* and *V*(*x*) the volume of the molten zone:

$$V(x) = \int_x^{x+w} A(x)dx$$

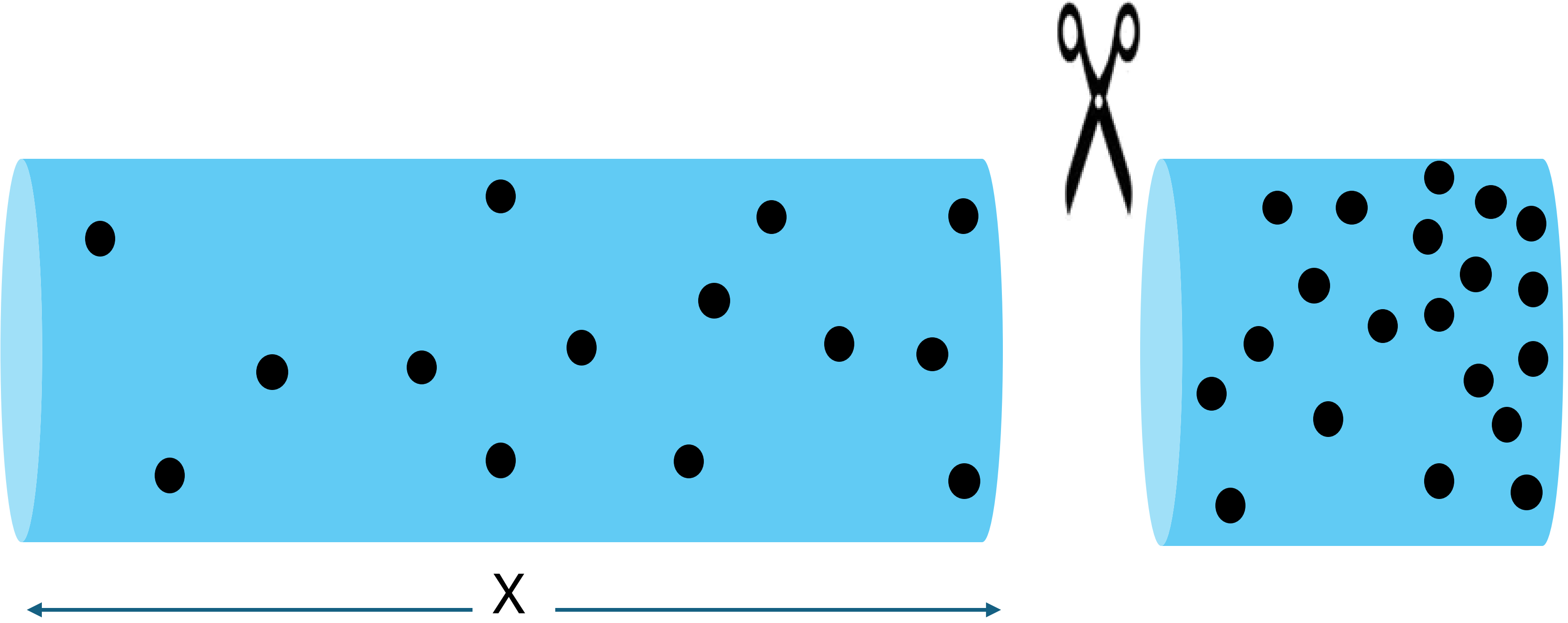
and the starting condition

$$C_n\,(0) = \frac{1}{V(0)}\int_0^w C_{n-1}(x)A(x)dx$$

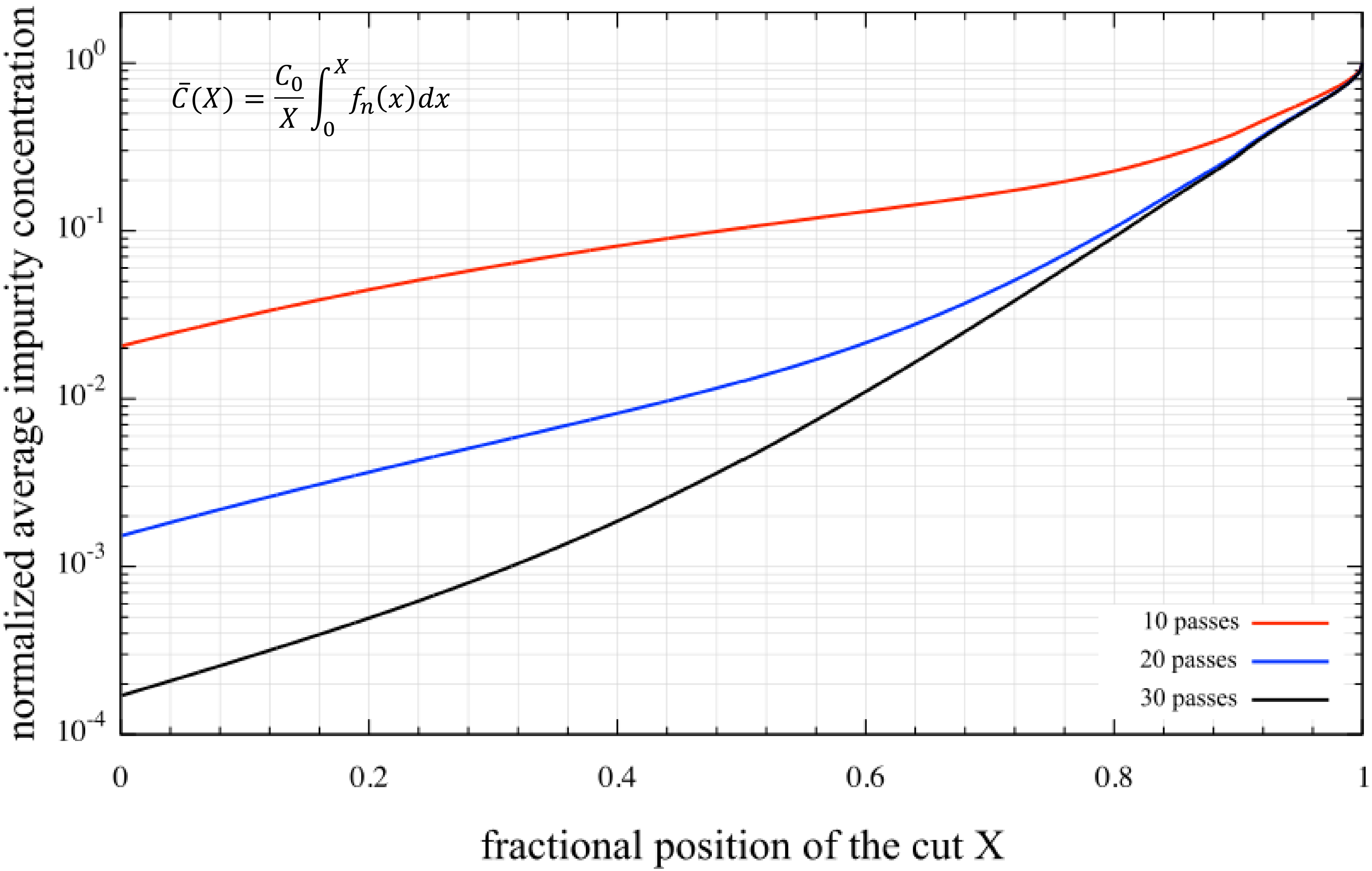
This equation includes also the tail, in which $V(x) = S \cdot (L-x)$ and $A(x+w)=0$ if $x>L-w$.

Cutting the edge: after refining the tail of the ingot is cut away and the rest of the ingot is shuttered and recast in the final crystal growth (normal freezing). The average contaminant concentration is a function of the cut

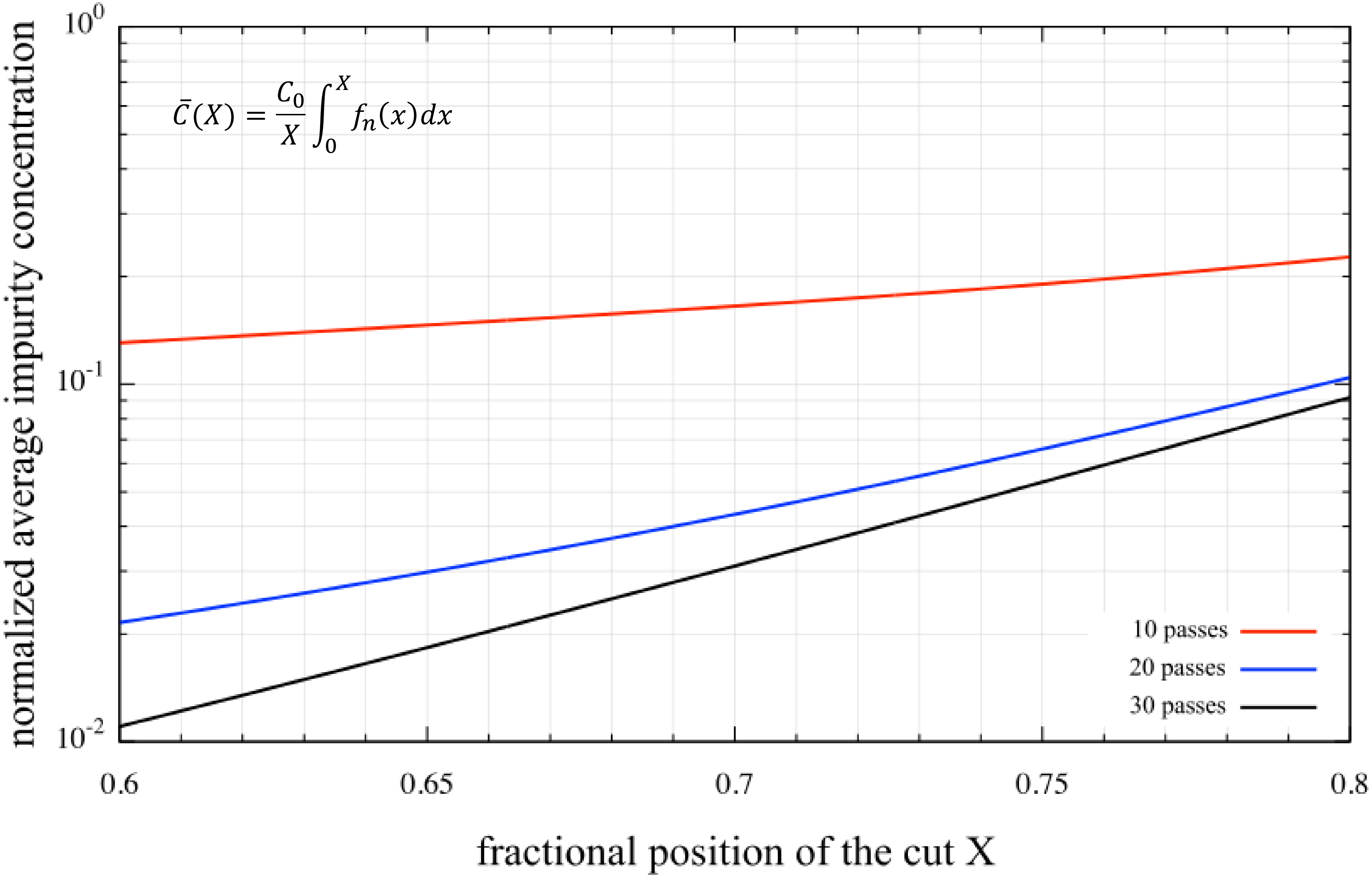
$$\bar{C}(X) = \frac{C_0}{X}\int_0^X f_n(x)dx$$

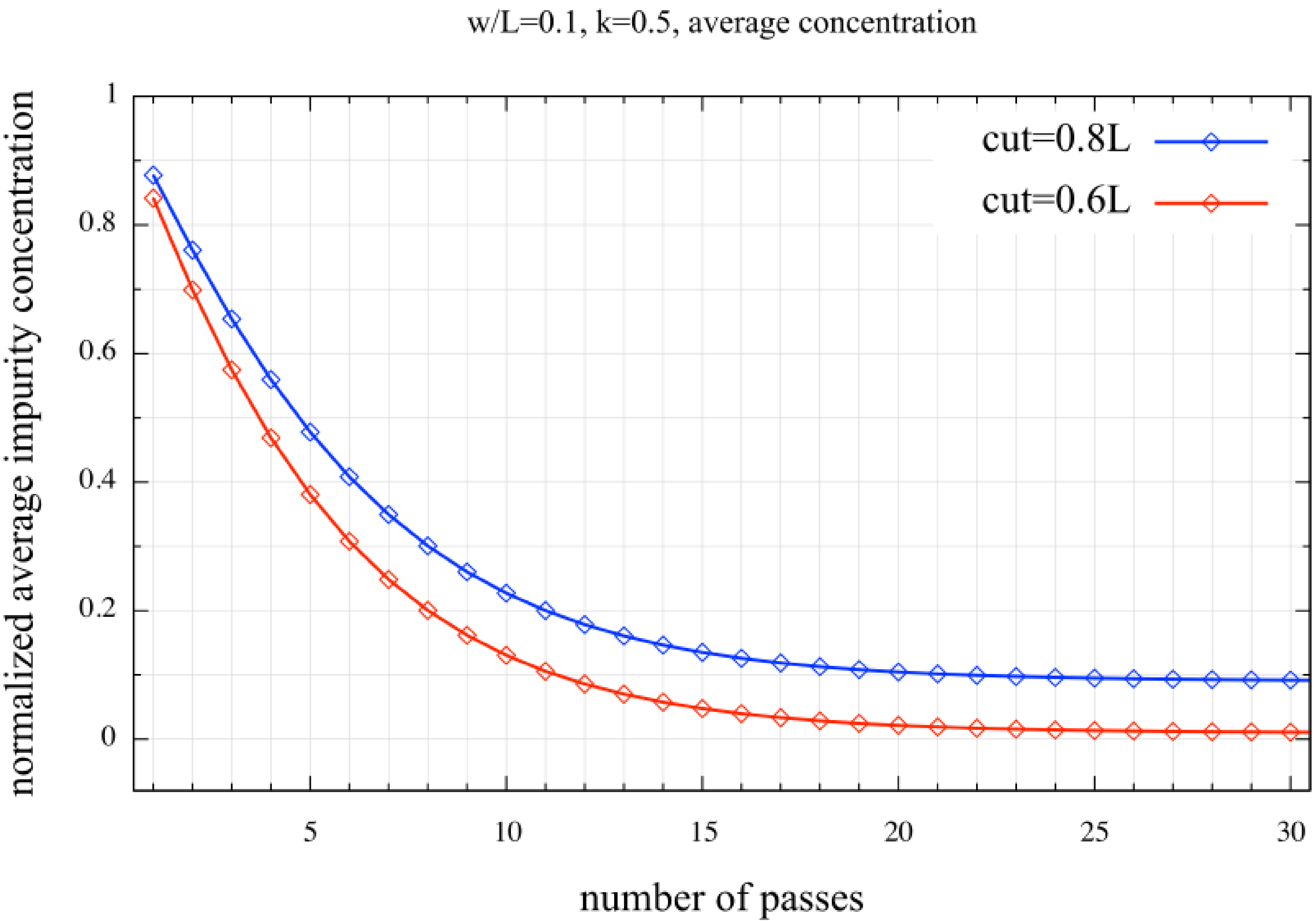


w/L=0.1, k=0.5, average concentration



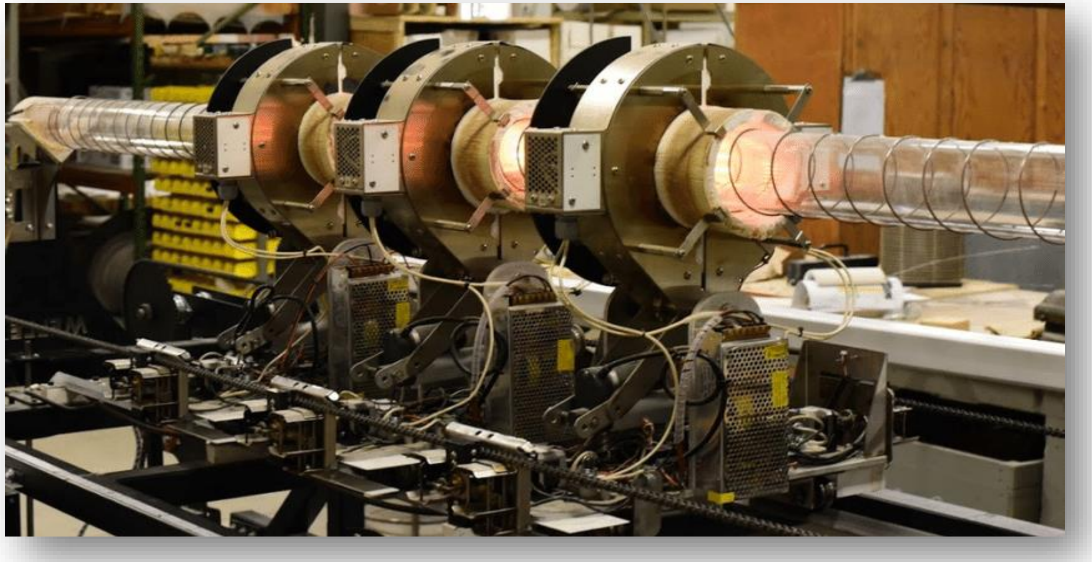
w/L=0.1, k=0.5, average concentration

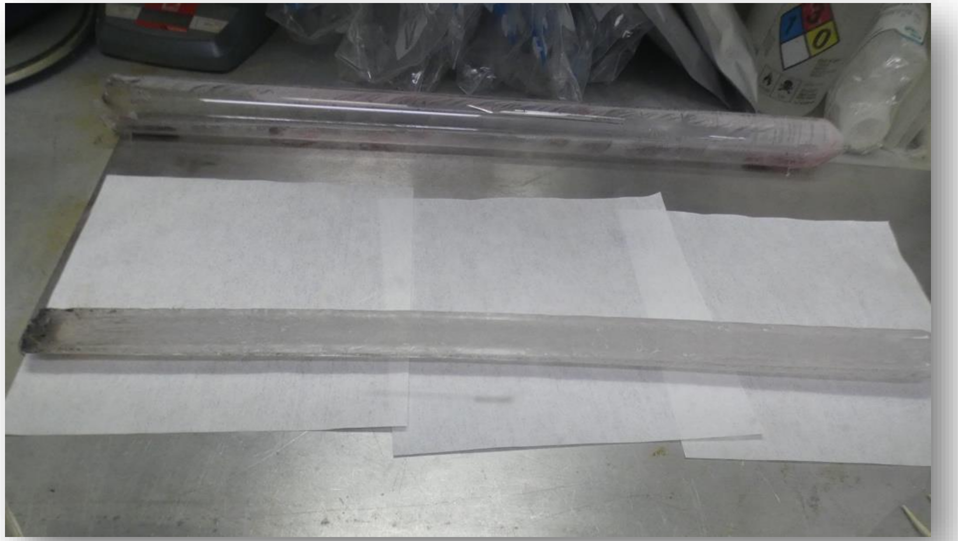



w/L=0.1, k=0.5, average concentration
cut=0.8L
cut=0.6L
normalized average impurity concentration
number of passes
1
0.8
0.6
0.4
0.2
0
5
10
15
20
25
30

Application to SABRE: ultrapure NaI crystals are necessary to compete with DAMA/LIBRA

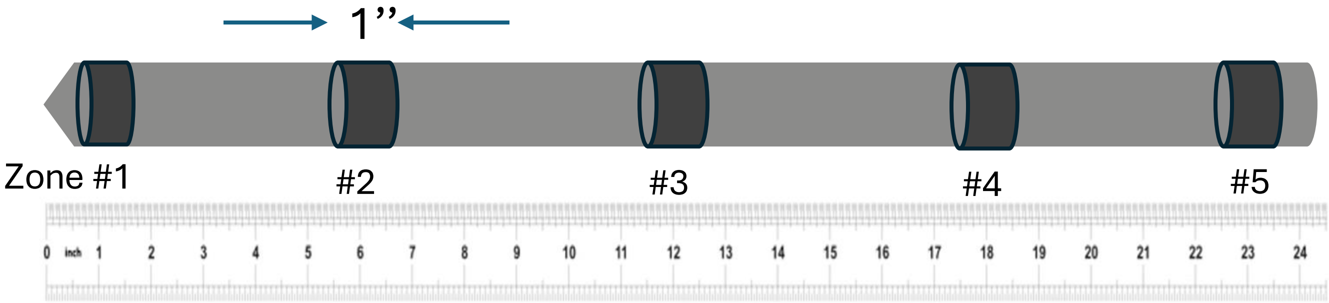
Radioclean NaI powder *Astrograde* by Sigma Aldrich (now Merck) is refined at Mellen company (Concord, NH)



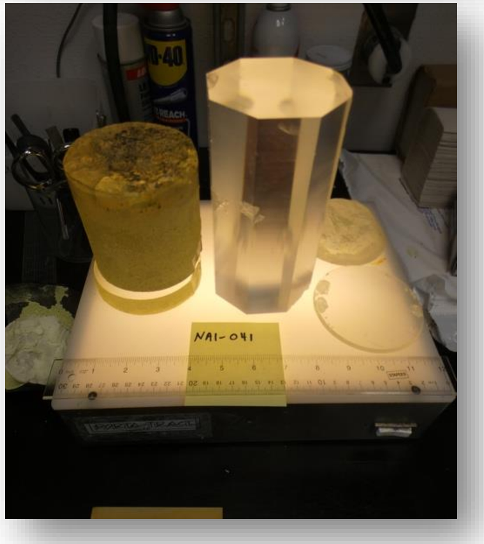


The purified (but raw) crystal is moved to Radiation Monitoring Device (Boston)

For each run 5 samples from ingot are taken at the position in figure and shipped at LSC (Canfranc) and Seastar for analysis



Final crystal is grown in vertical Bridgman method in fused silica vessels (*normal freezing*)



ZR Run 1 (26 passes, 1.5 inch/h, ampoule with Carbon coating, powder: 76650)

Sample	^{39}K [ppb]		^{65}Cu [ppb]		^{85}Rb [ppb]		^{133}Cs [ppb]		^{138}Ba [ppb]		^{88}Sr [ppb]			^{208}Pb [ppb]		
	LSC	Seast	LSC	Seast	LSC	Seast	LSC	Seast	LSC	Seast	Seast	LNGS	LSC	LSC	Seast	LNGS
powder	14.4	6.7	<5	<4	<0.8	<0.4	11	19	<0.6	0.18	1			2	1.6	
Zone #1	<4	<4	<5	<3	<0.8	<0.4	<0.3	<2	<0.5	<0.3	367		350	5.1	3.6	
Zone #2	<4	<4	<5	<3	<0.8	<0.4	<0.3	<2	0.8	<0.3	287	180	93	2.6	2.9	2.5
Zone #3	6.7	<4	<5	<3	<0.8	<0.4	0.4	<2	0.8	<0.3	86			<1	1.8	
Zone #4	40	6.3	<5	<3	<0.8	<0.4	0.4	<2	3.8	<0.3	41	20		<1	1.2	1.6
Zone #5	540	275	234	150	1.3	<0.4	447	570	10	3.7	10	4	4.7	1.9	0.95	0.9

The two main contaminants for the experiment are ^{40}K and ^{210}Pb

Statistical analysis: in order to find the segregation constants *k* for the various contaminant previous data must be fitted with the ZR model discussed previously.

The fitting procedure procedure must face three problems

- The first zones present only upper limits due to the sensitivity of the procedure of measurement
- The measures are carried out on grains taken randomly in each zone after crunching. For this reason, the measures have a uniform uncertainty on the x position
- The error on the measures is unknown. We assume conservatively a 20% gaussian error on the measures (dominated by systematics) while for upper limits we assume a uniform probability for all values smaller that the limit

For these reasons, a maximum likelihood procedure is more appropriate for fitting rather than a χ^2.

Fitting procedure: we can write the likelihood function as

$$L(k, C_0) = Pr(C_0) \times \prod_{z=1}^{5} \mathcal{P}_z(k, C_0)$$

where $\mathcal{P}_z$ are the probabilities in each zone and *Pr* is a prior. For zones in which we have a measure C_z^{exp}

$$\mathcal{P}_z(k, C_0) \propto \int_{x_z - \frac{\delta_z}{2}}^{x_z + \frac{\delta_z}{2}} \exp\left[-\frac{\left(C_z^{exp} - C_0 f_n(x)\right)^2}{2\sigma_z^2}\right] dx$$

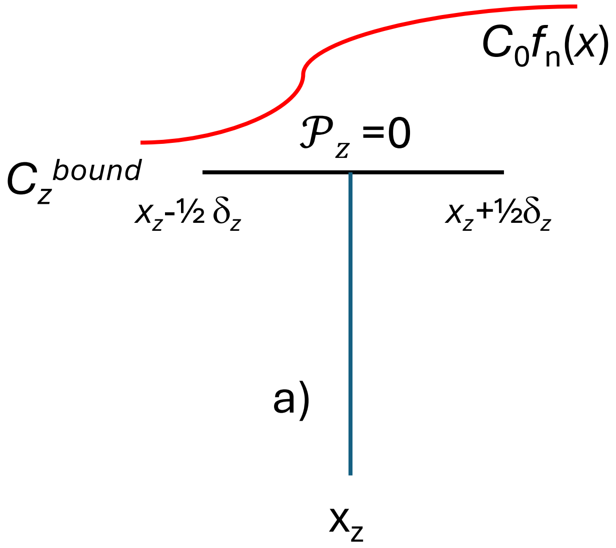
with x_z and δ_z central value and width of the *z*-th bin, σ_z estimated error on the measure (we fix $\sigma_z = 0.2 \times C_z^{\mathrm{exp}}$) and *n* number of passes. We thus consider all the values $x \in [x_z - ½\delta_z, x_z + ½\delta_z]$ equiprobable.

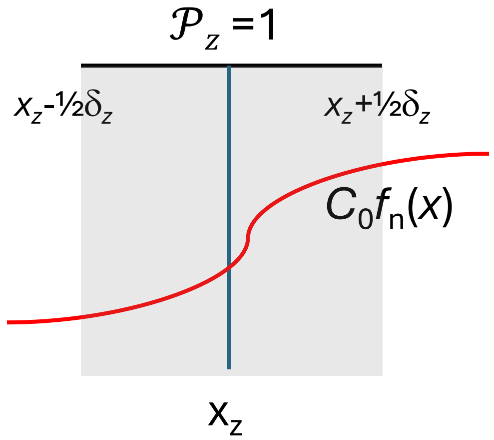
For the zones in which we have only an upper bound C_z^{bound} we have:

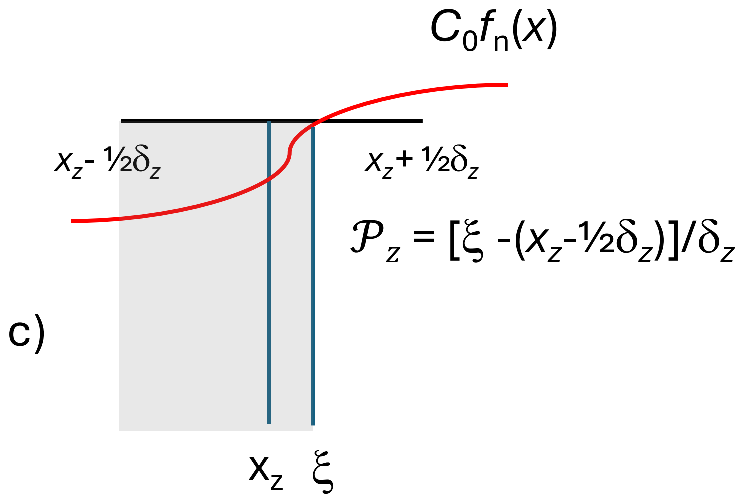
a) If $C_0 f_n(x) > C_z^{bound}$ $\forall\, x \in [x_z - \tfrac{1}{2}\delta_z, x_z + \tfrac{1}{2}\delta_z]$ we put $\mathcal{P}_z = 0$ since the theoretical values cannot be higher than the upper value

b) Conversely, if $C_0 f_n(x) < C_z^{bound}$ $\forall\, x \in [x_z - \tfrac{1}{2}\delta_z, x_z + \tfrac{1}{2}\delta_z]$ we have $\mathcal{P}_z = 1$ since each value of x in the interval is equiprobable

c) If $\exists \xi \in [x_z - \tfrac{1}{2}\delta_z, x_z + \tfrac{1}{2}\delta_z]$ with $C_0 f_n(\xi) = C_z^{bound}$ we can consider only the fraction of bin in which the curve is below the bound. E.g., if $f_n(x)$ is increasing $\mathcal{P}_z = [\xi - (x_z - \tfrac{1}{2}\delta_z)]/\delta_z$







Finally, in order to avoid that the fitted value of C_0 deviate too much from the value measured in the powder we multiply by a prior function

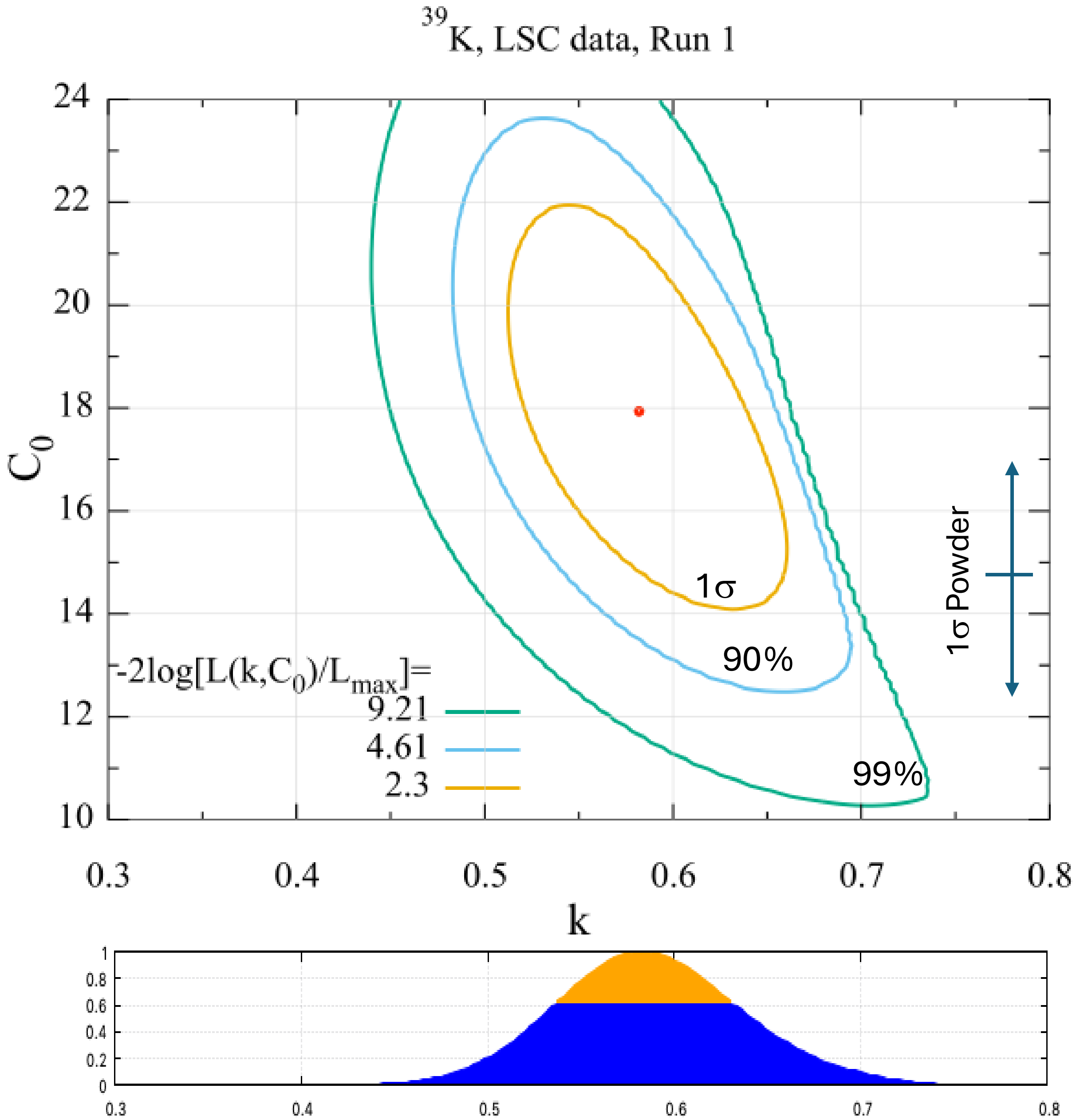
$$Pr(C_0) = \exp\left[-\frac{\left(C_0 - C_{powder}\right)^2}{2\sigma_{powder}^2}\right]$$

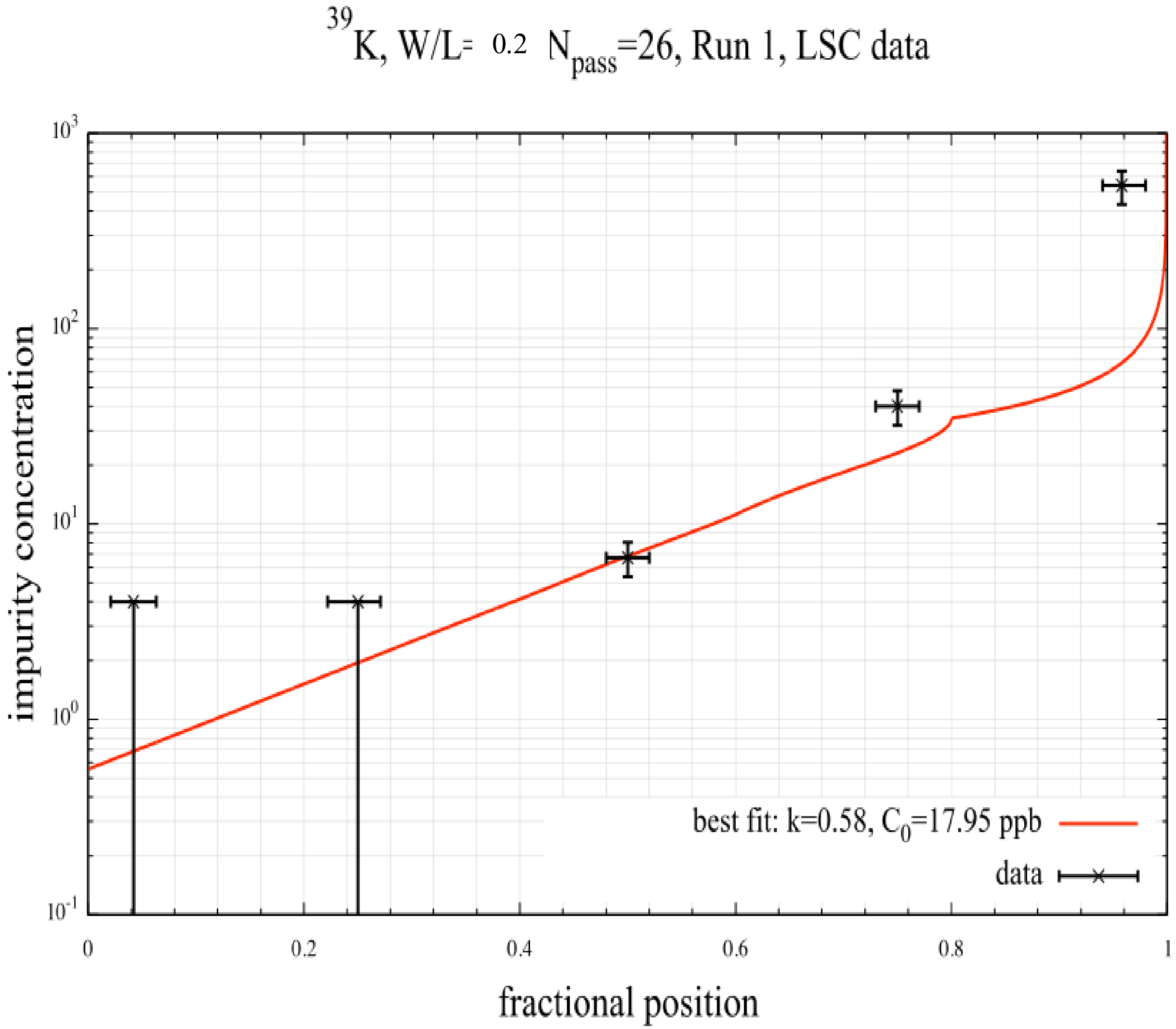
(we assume $\sigma_{powder}=0.2\times C_{powder}$).

We define the likelihood ratio function

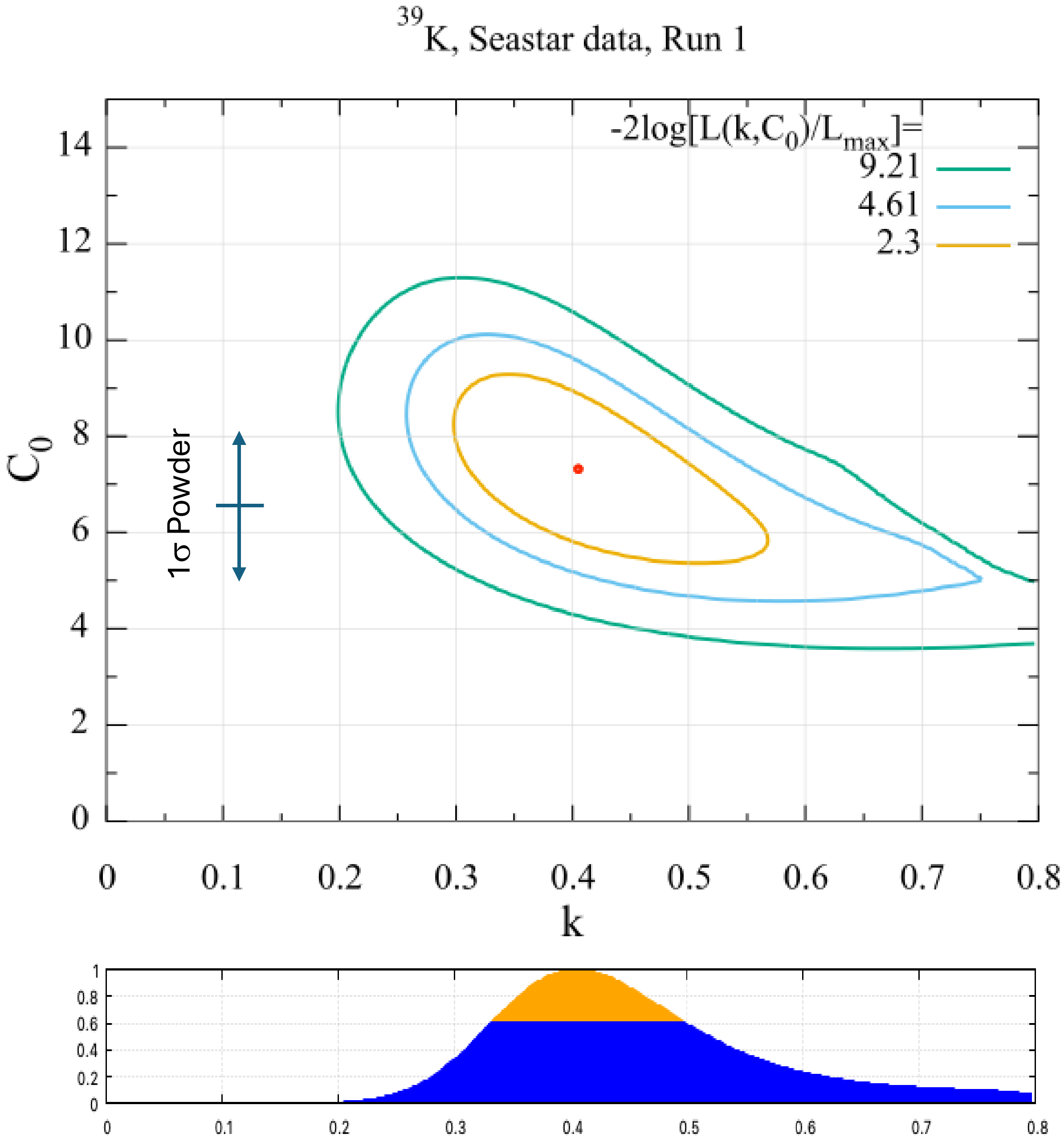
$$\lambda(k, C_0) = -2\log\left[\frac{L(k, C_0)}{L\left(\hat{k}, \hat{C}_0\right)}\right]$$

were $\hat{k}$ and $\hat{C}_0$ are the value that maximize the likelihood (best fit values). According to the Wilk’s theorem this function behaves approximatively like a χ^2.

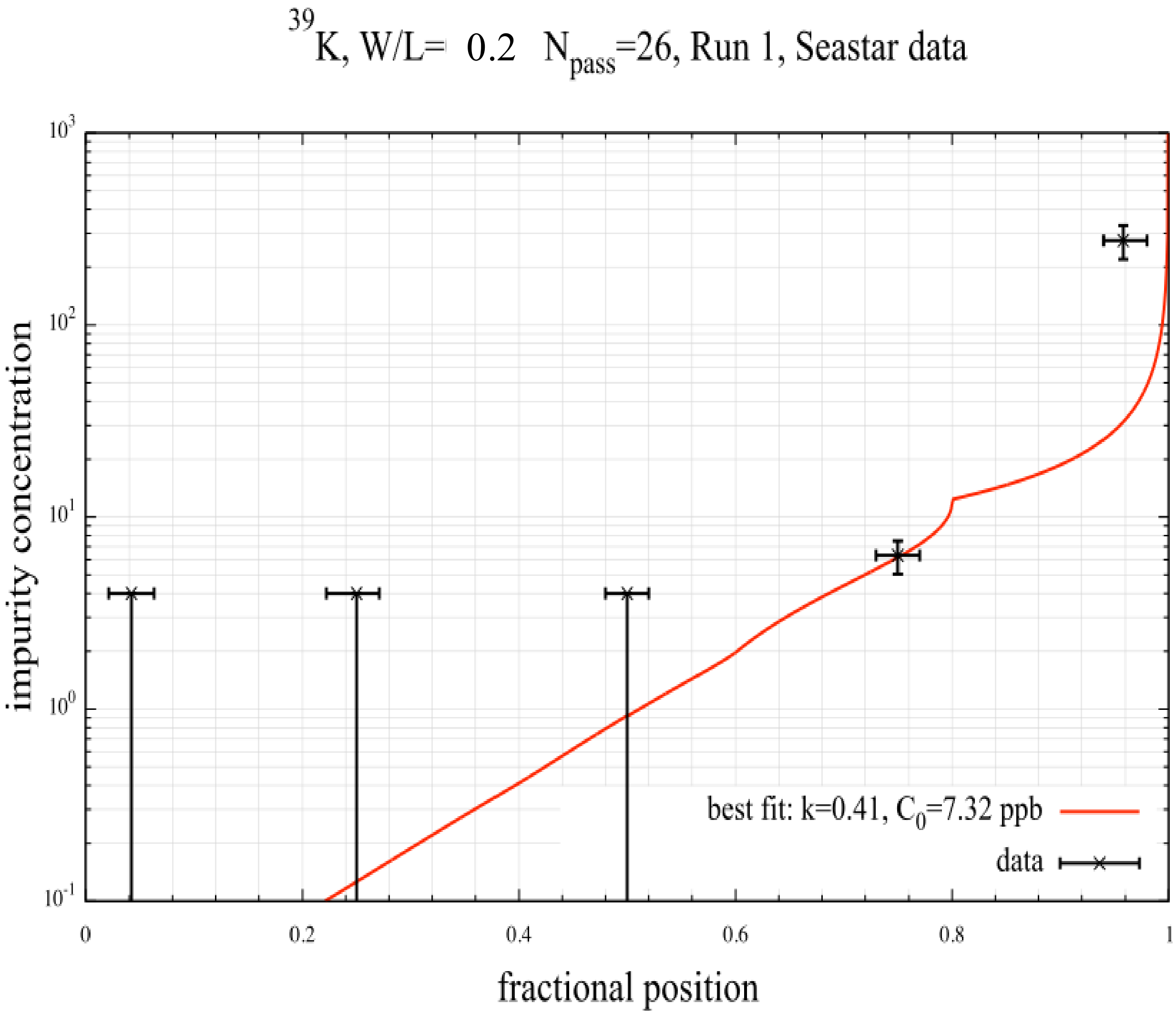

^{39}K, LSC data, Run 1
C_0
24
22
20
18
16
14
12
10
0.3
0.4
0.5
0.6
0.7
0.8
k
1σ
90%
99%
1σ Powder
-2log[L(k,C$_0$)/L$_{max}$]=
9.21
4.61
2.3
1
0.8
0.6
0.4
0.2
0


^{39}K, W/L= 0.2 N$_{pass}$=26, Run 1, LSC data
impurity concentration
10^3
10^2
10^1
10^0
10^{-1}
0
0.2
0.4
0.6
0.8
1
fractional position
best fit: k=0.58, C$_0$=17.95 ppb
data

k=0.58±0.05 @ 1σ



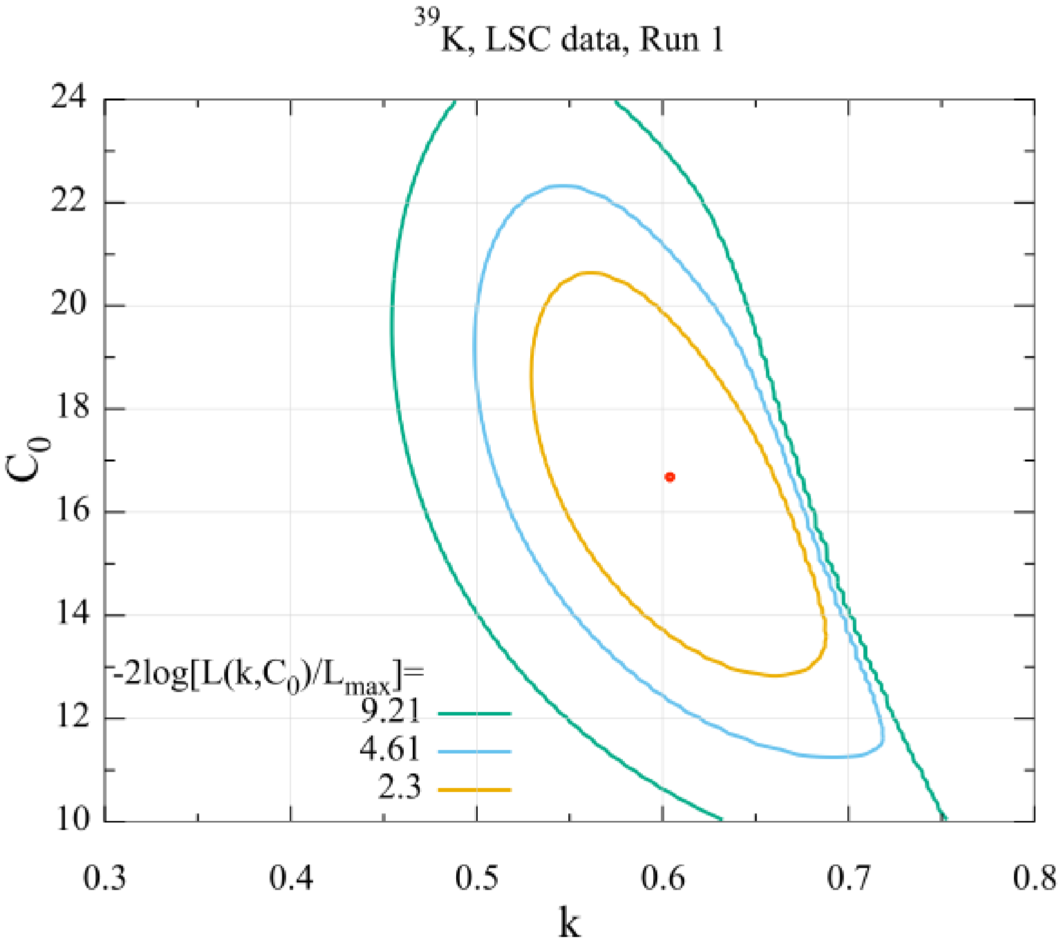
^{39}K, Seastar data, Run 1

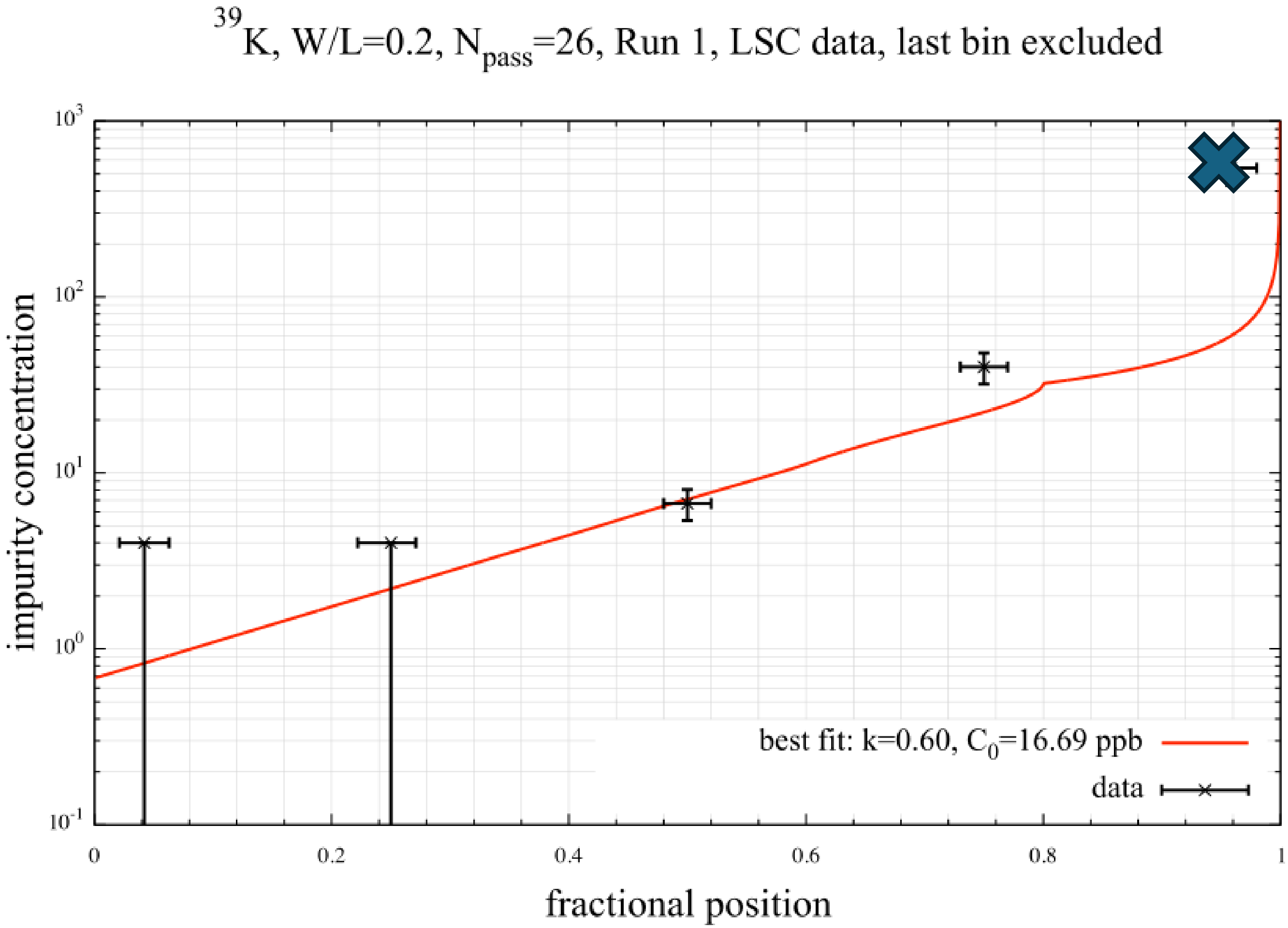


^{39}K, W/L= 0.2 N_{pass}=26, Run 1, Seastar data

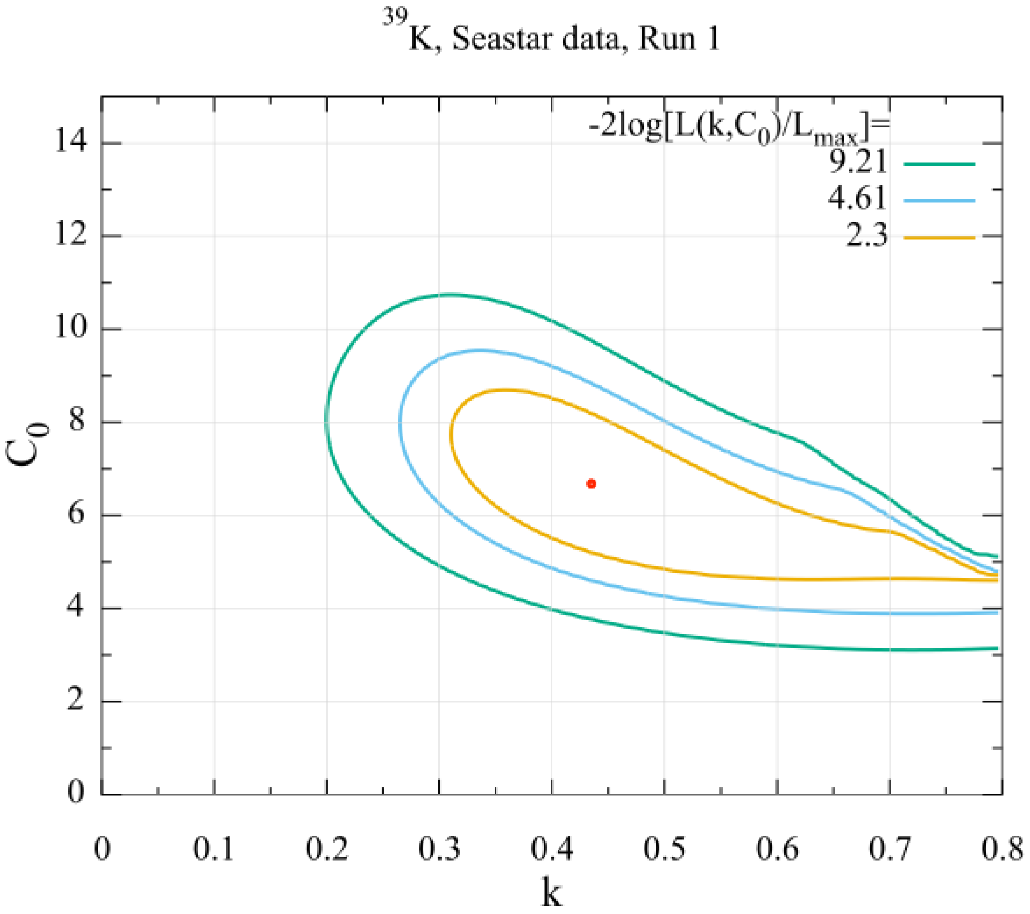
k=0.41±0.08 @ 1σ

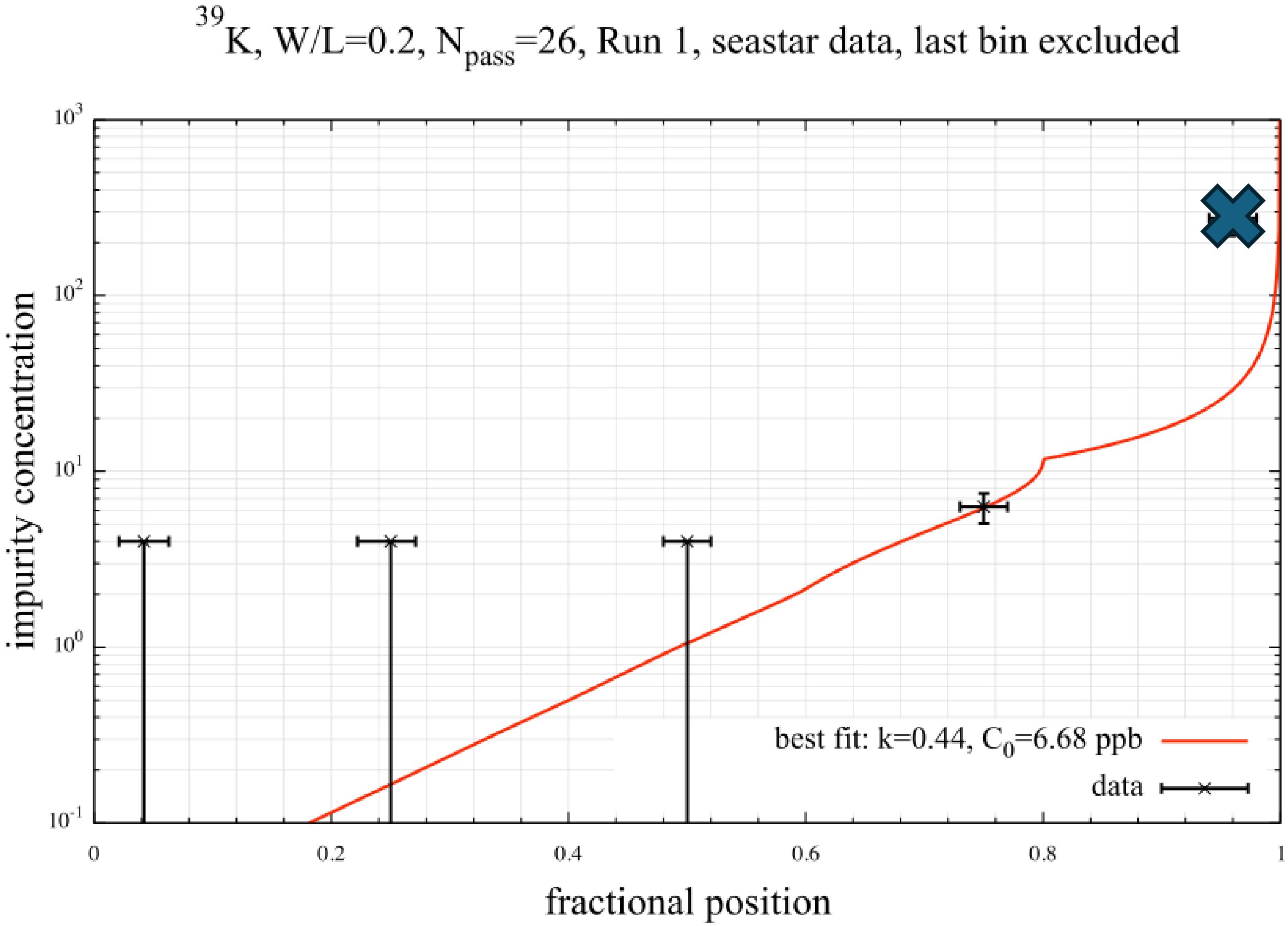
Excluding last bin doesn't change too much the results…

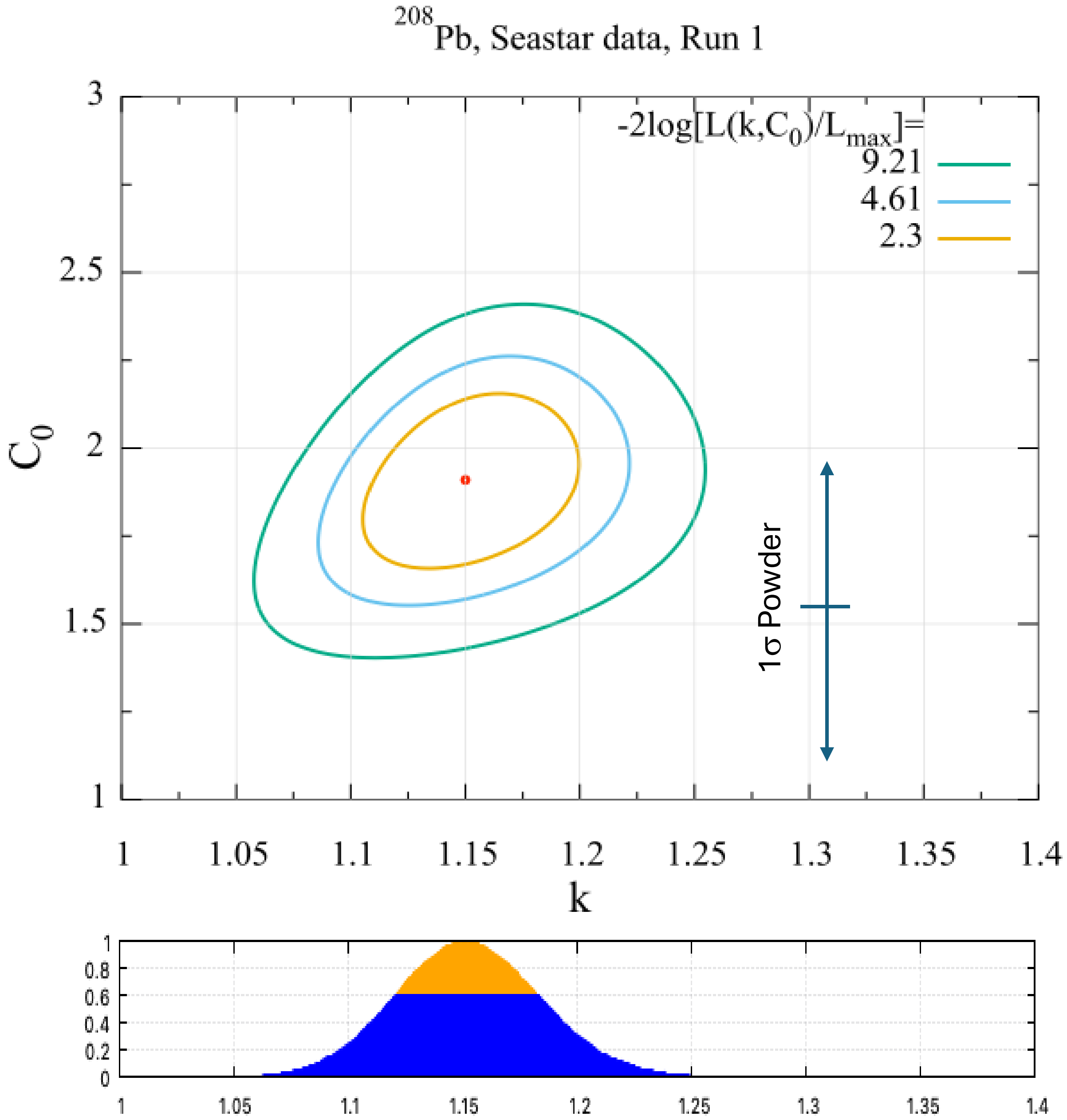

^{39}K, LSC data, Run 1

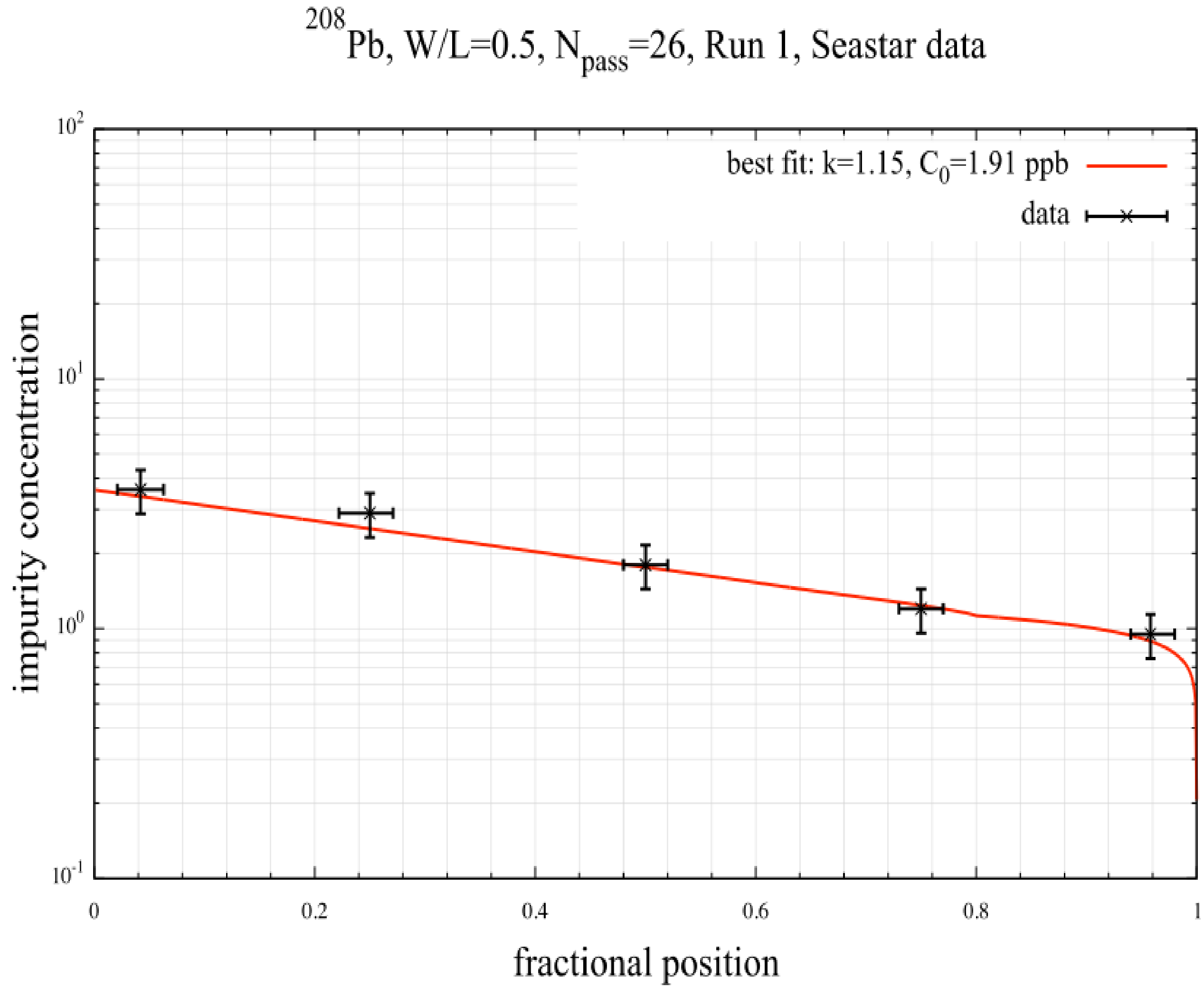

^{39}K, W/L=0.2, N_{pass}=26, Run 1, LSC data, last bin excluded

Excluding last bin doesn't change too much the results…

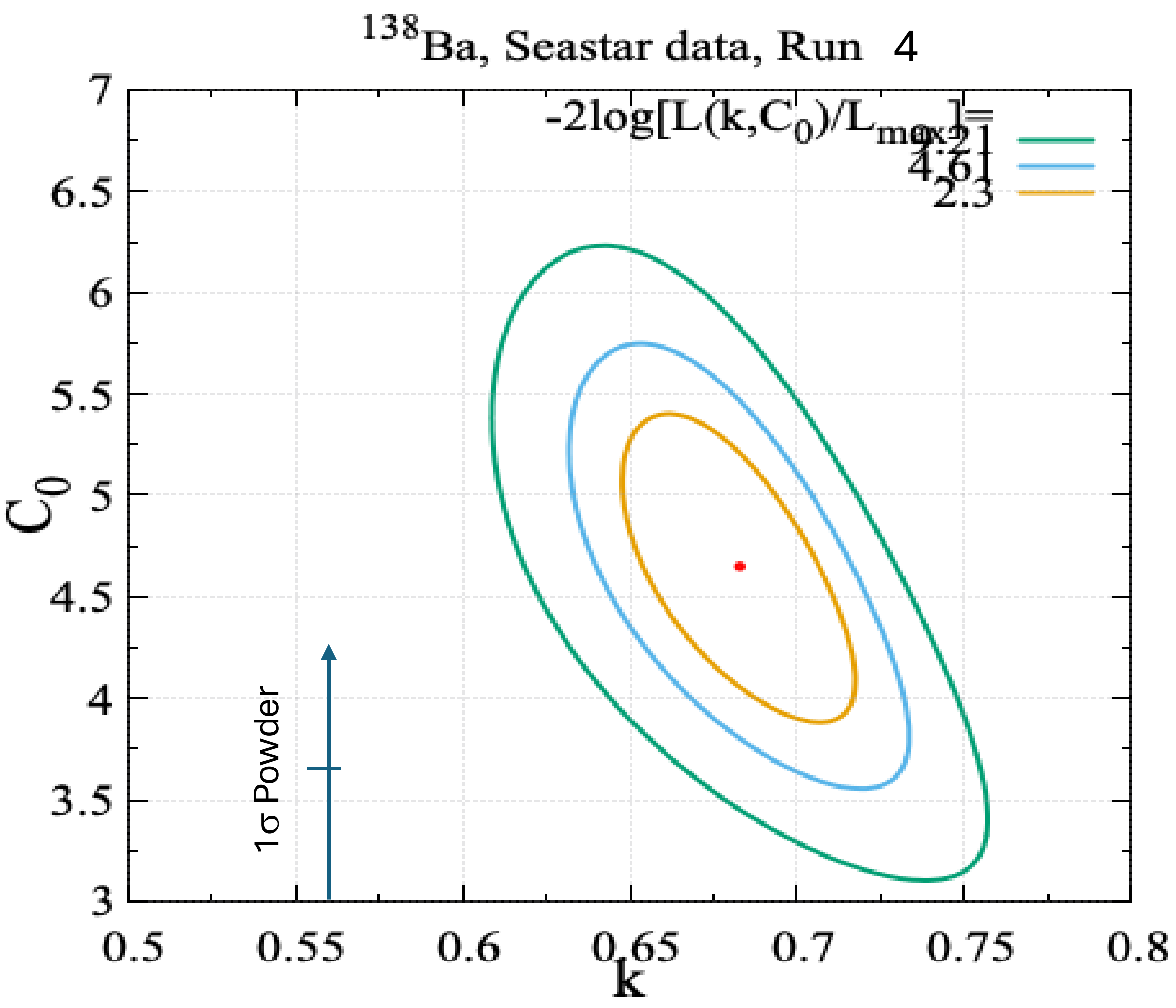




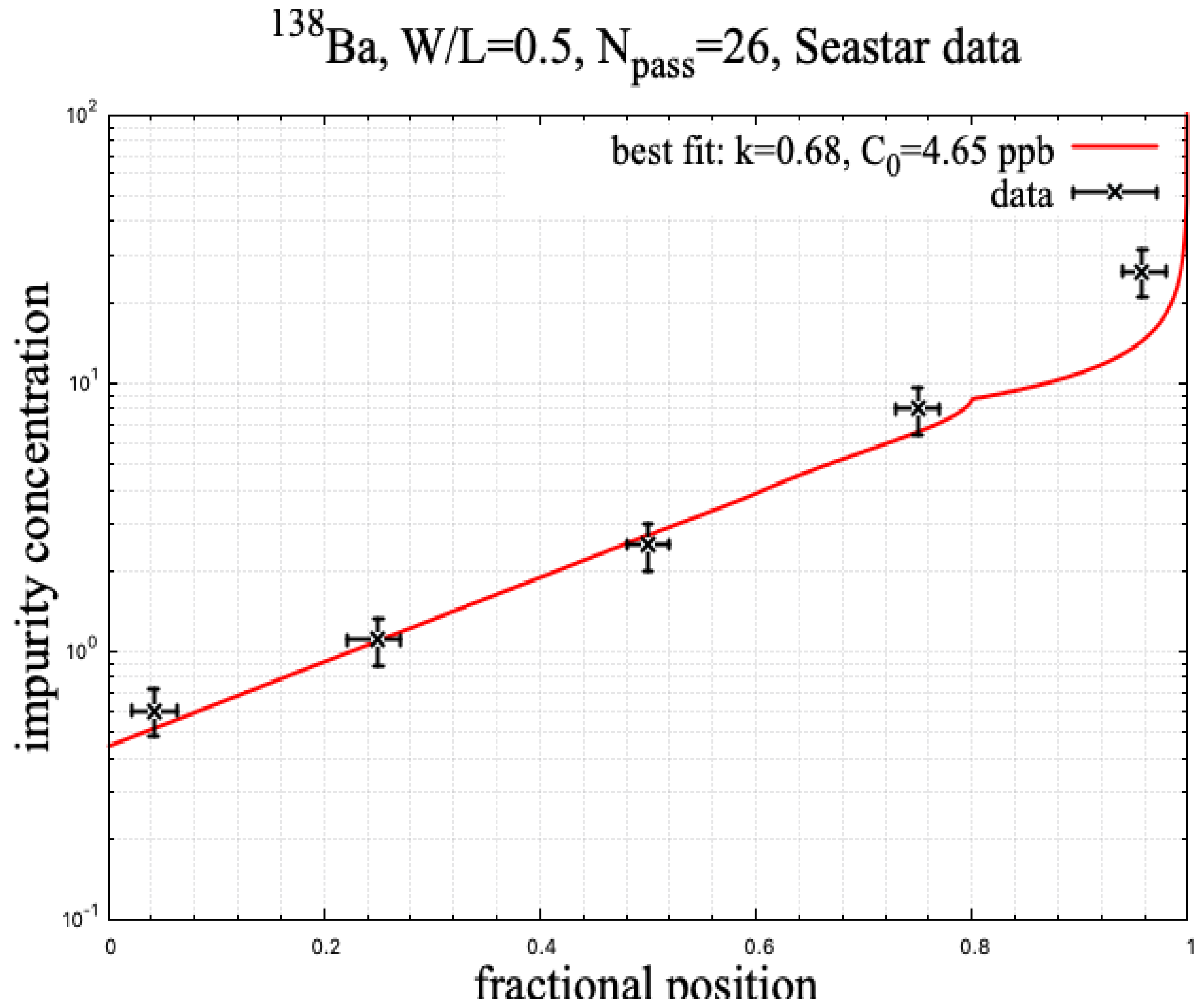

^{208}Pb, Seastar data, Run 1


^{208}Pb, W/L=0.5, N_{pass}=26, Run 1, Seastar data

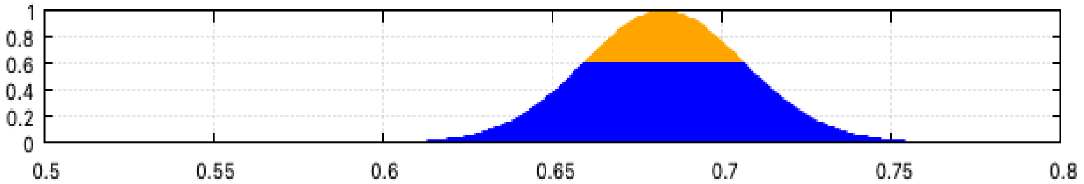
k=1.15±0.03 @ 1σ



^{138}Ba, Seastar data, Run 4
-2log[L(k,C$_0$)/L$_{max}$]=
9.21
4.61
2.3
C_0
7
6.5
6
5.5
5
4.5
4
3.5
3
1σ Powder
k
0.5
0.55
0.6
0.65
0.7
0.75
0.8



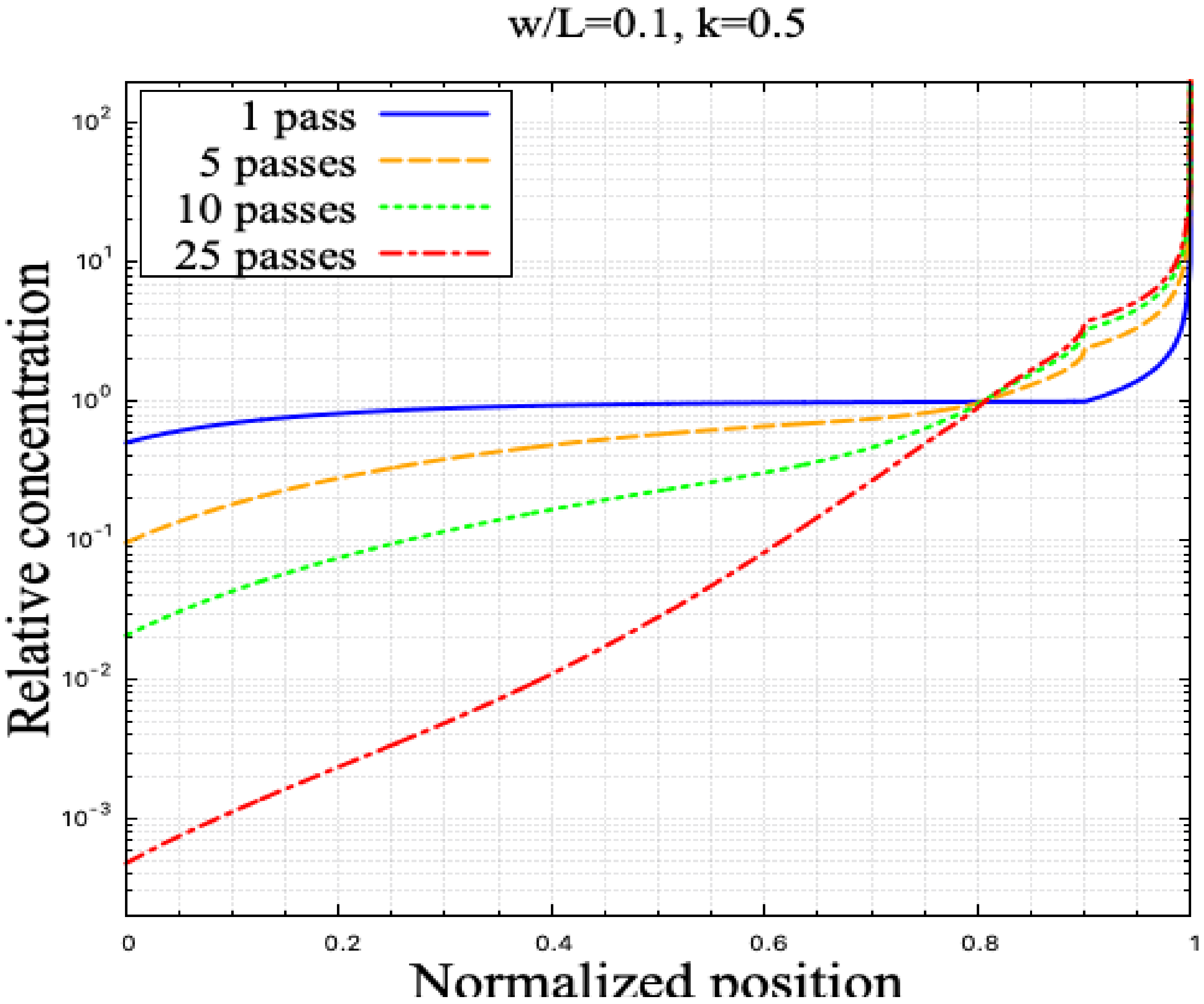
^{138}Ba, W/L=0.5, N_{pass}=26, Seastar data
best fit: k=0.68, C_0=4.65 ppb
data
impurity concentration
10^2
10^1
10^0
10^{-1}
fractional position
0
0.2
0.4
0.6
0.8
1

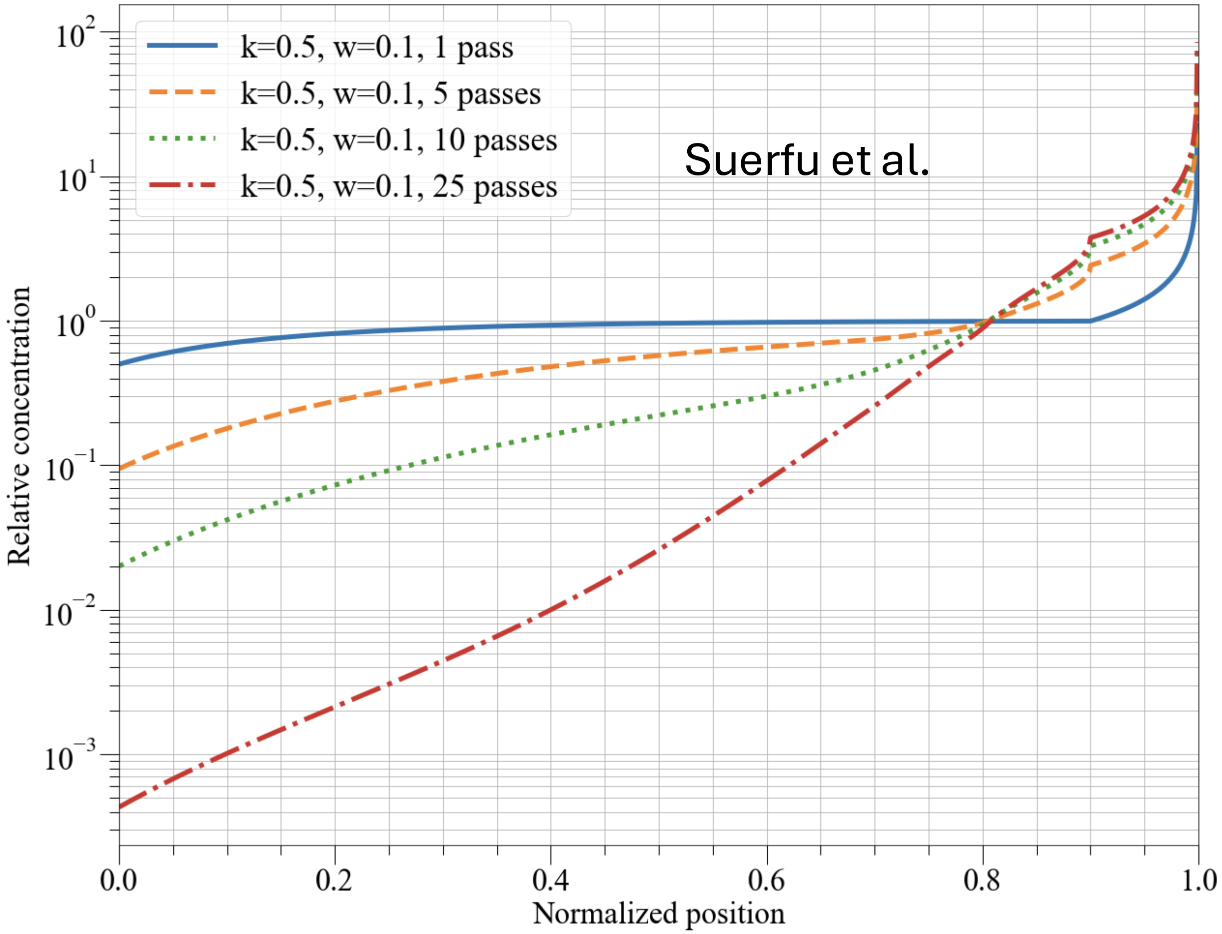


1
0.8
0.6
0.4
0.2
0
0.5
0.55
0.6
0.65
0.7
0.75
0.8

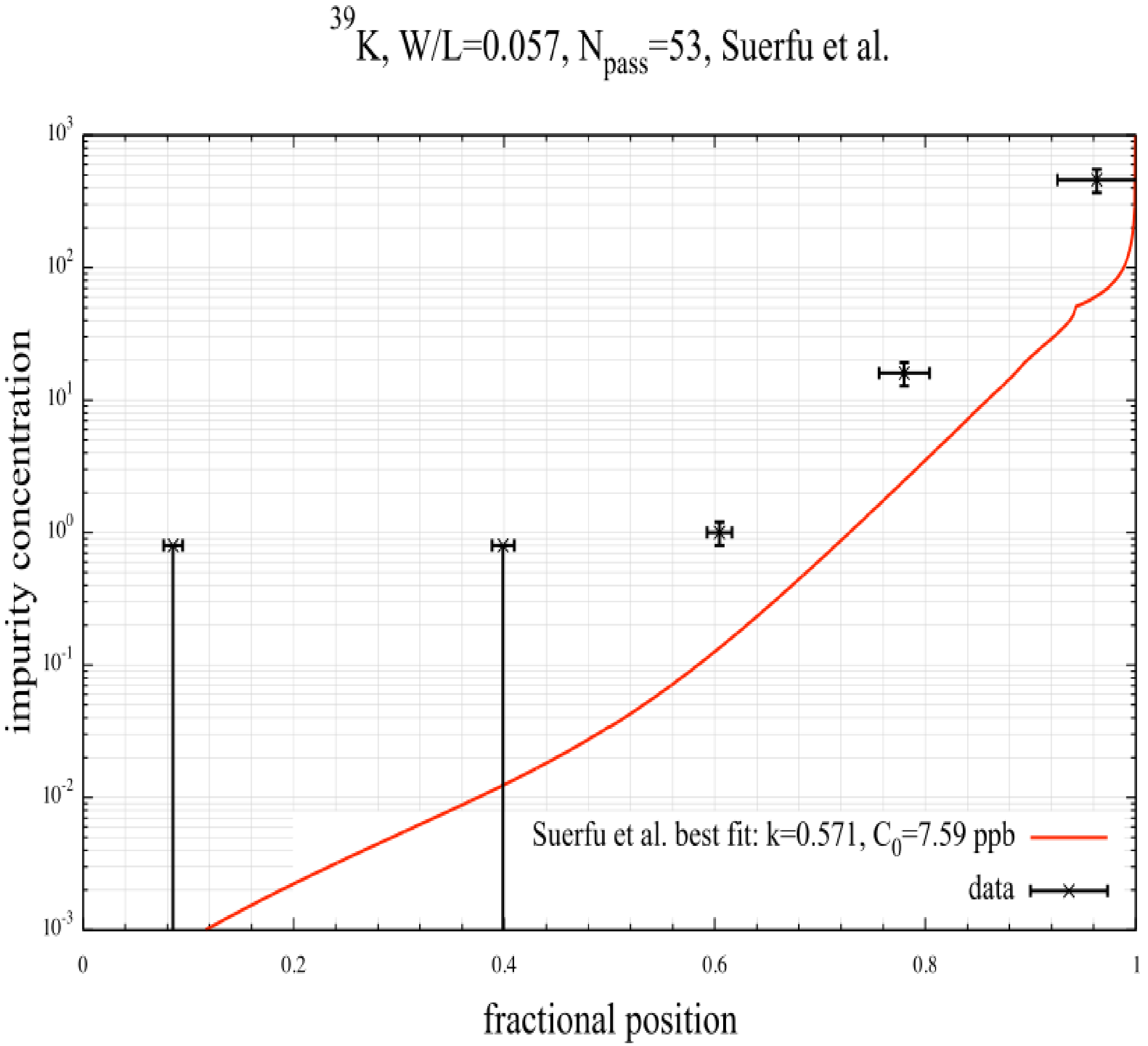
k=0.68±0.02 @ 1σ

Comparison with literature: we tried to reproduce the analysis done by *Suerfu, Calaprice and Souza* [Phys. Rev. Appl. **16**, 014060, (2021)]. We can reproduce exactly their Fig. 4…





...however, we cannot reproduce their results in Fig. 5!


^{39}K, W/L=0.057, N_{pass}=53, Suerfu et al.

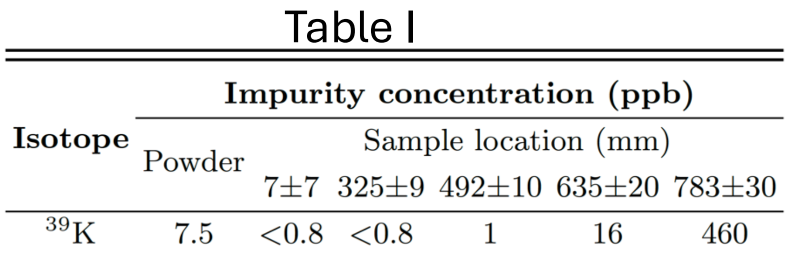
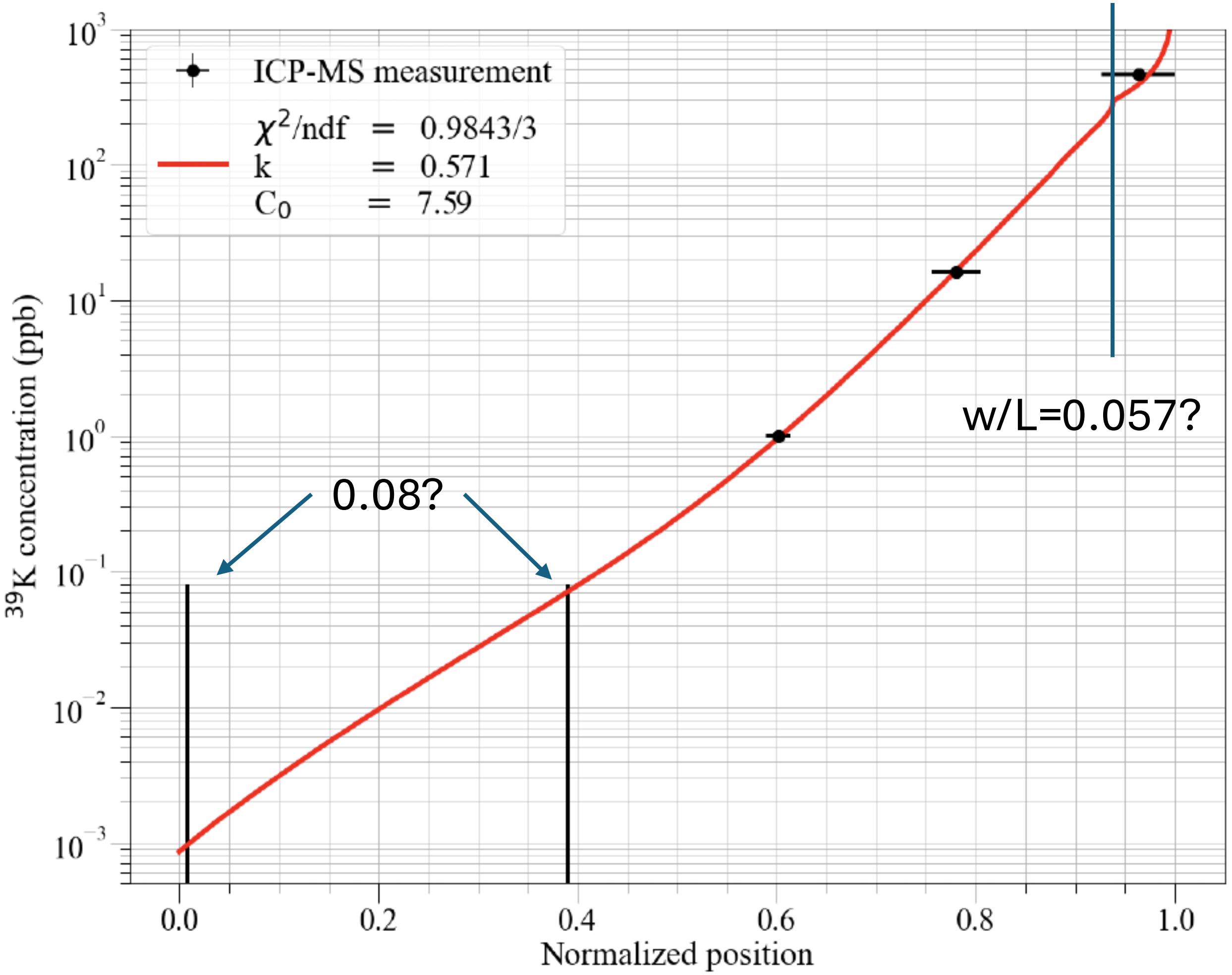


Table I

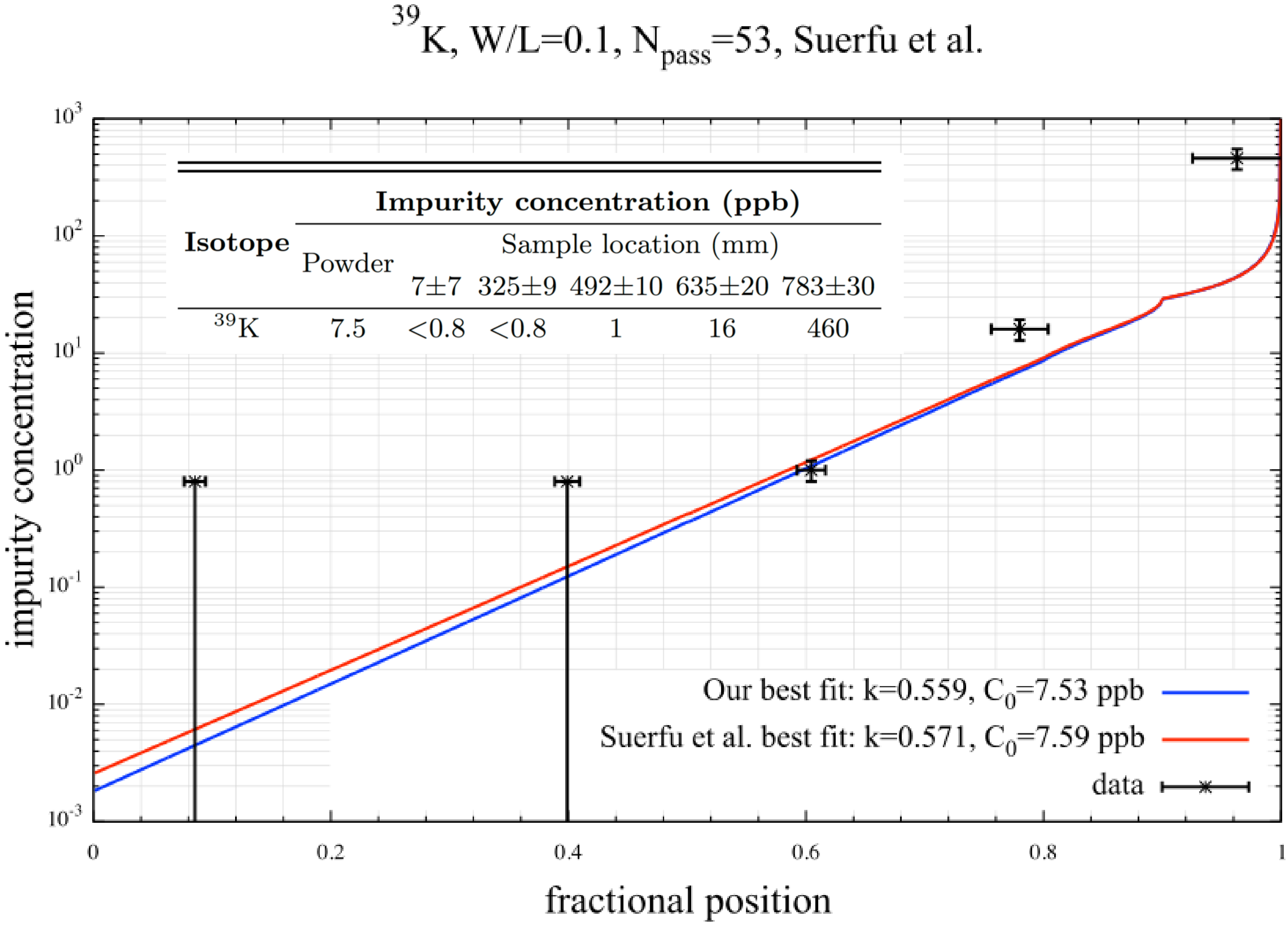
Isotope	Impurity concentration (ppb)					
	Powder	Sample location (mm)				
		7±7	325±9	492±10	635±20	783±30
^{39}K	7.5	<0.8	<0.8	1	16	460



0.08?

w/L=0.057?

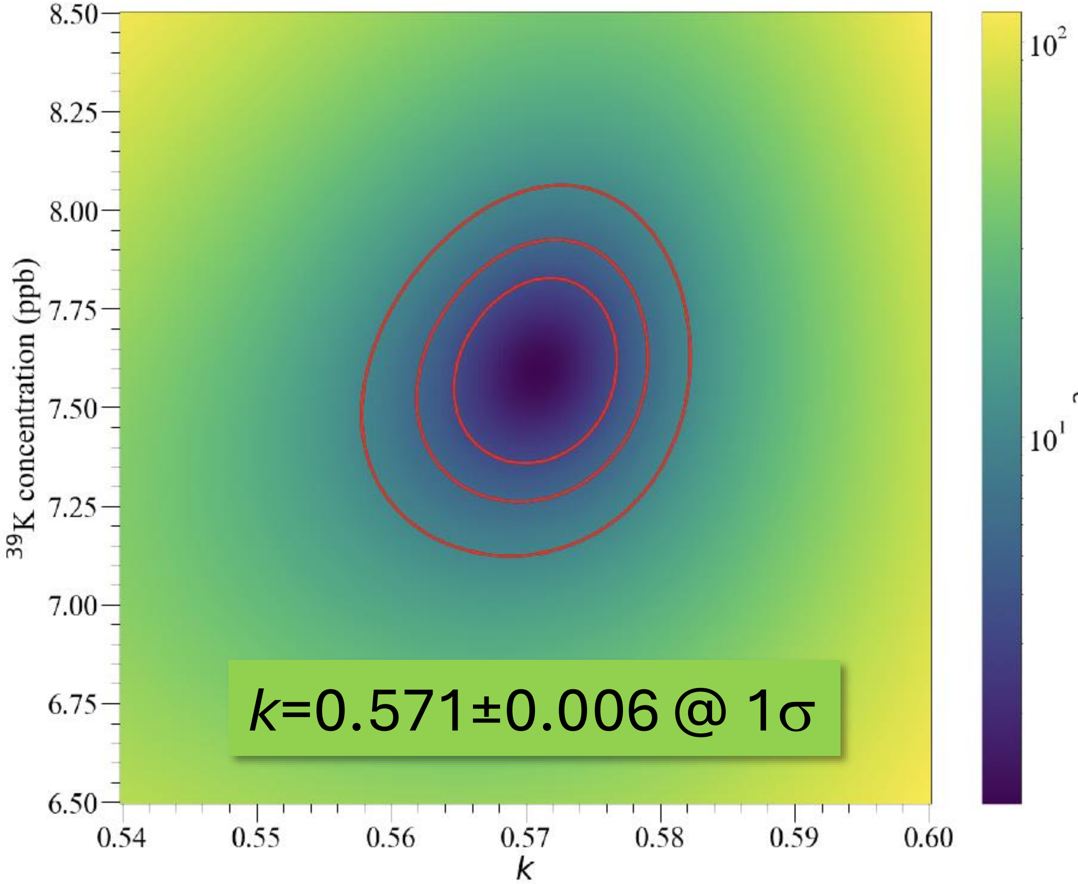
Anyway, using their data we found more or less the same best fit. We assume again a 20% error on measure (in Suerfu et al. the error is not specified). We also assumed the “a posteriori” error quoted by Suerfu et al. on C_0 (5.3% error).



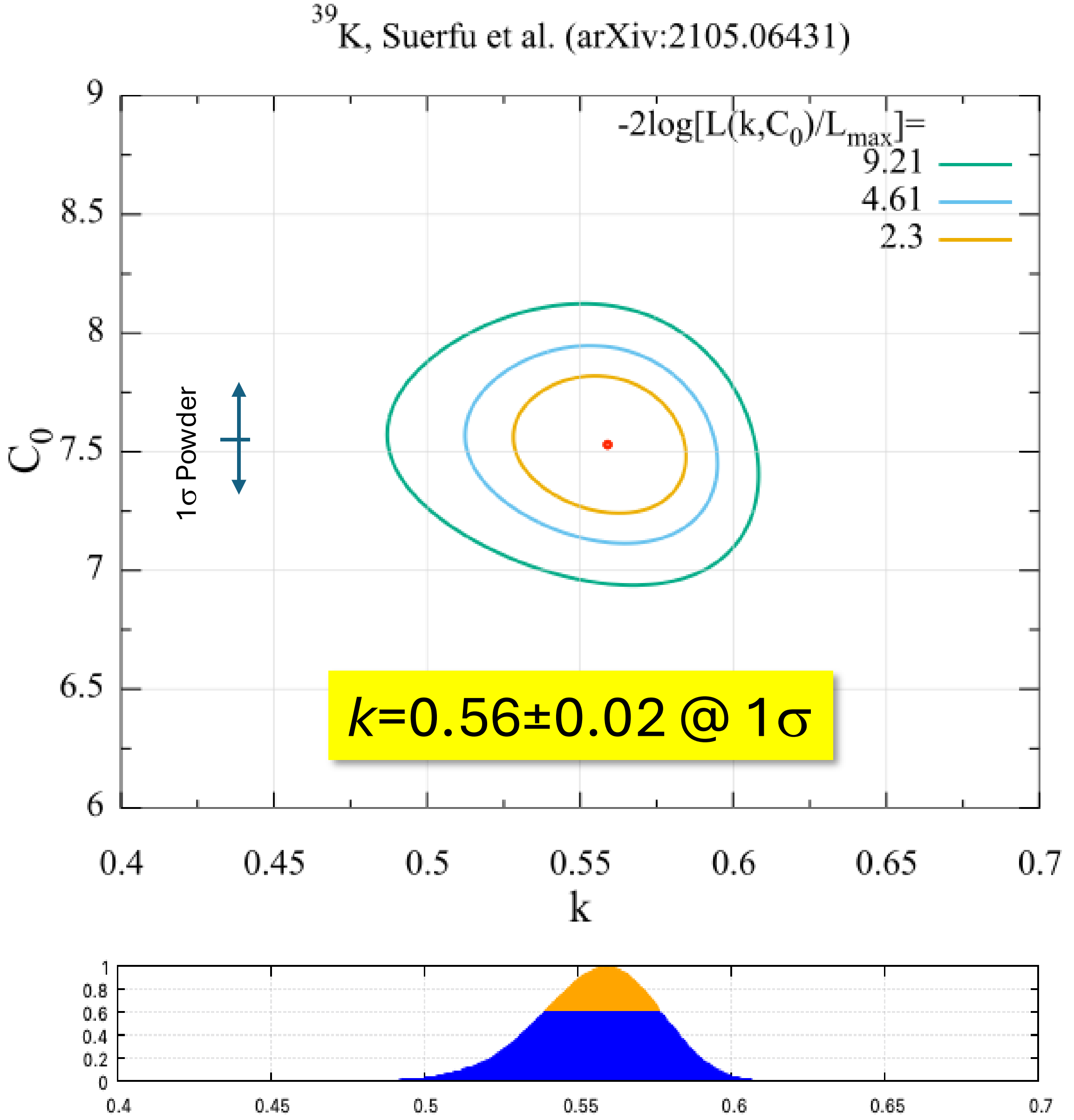
^{39}K, W/L=0.1, N_{pass}=53, Suerfu et al.

	Impurity concentration (ppb)					
Isotope	Powder	Sample location (mm)				
		7±7	325±9	492±10	635±20	783±30
^{39}K	7.5	<0.8	<0.8	1	16	460

Fig. 6 by Suerfu *et al*. vs our analysis.
Notice that the scales are different



k=0.571±0.006 @ 1σ



k=0.56±0.02 @ 1σ

We cannot reproduce the analysis by Suerfu *et al*. due to lack of information on the analysis procedure and some incongruences in their figures. The errors on *k* and C_0 seem to be underestimated.

Thank you for your attention

This work has been performed in collaboration with

- Gabriella Cataldi
- Samina Zuhra
- Sanagul Khattak
- Chemseddine Ananna
- Maria Luisa De Giorgi