

Supporting Information:
Accounting for Unknown Systematic Errors in Rietveld Refinements:
A Bayesian Statistics Approach

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Table S1: Parameters of the priors used in the Bayesian fits of the error-free simulated neutron (ND) and X-ray (XRD) diffraction data.

	σ_δ	$l_\delta, \text{deg.}^{-1}$	k_μ	E_μ	k_β	E_β
Random choice, ND	0.08	0.25	20	7	1	7
Random choice, XRD	0.015	0.07	20	7	1	7
Optimal choice, ND	0.005	0.4	10^5	7	10^3	7
Optimal choice, XRD	0.001	0.1	10^5	7	10^3	7

Table S2: Estimates of the structural parameters and their uncertainties (± 1 esd) for PbSO₄ obtained using a combined fitting of the ND and XRD simulated data. For the Bayesian fits of the error-free data, the parameters of the priors are specified in Table S1. The optimal parameters of the priors for the ND and XRD data containing the multiplicative error were set at $k_\mu=1$ and $E_\mu=15$.

	True values	Error-free data		Data with multiplicative errors	
		Standard fit	Bayesian fit, random parameters	Bayesian fit, optimal parameters	Standard fit
$dx \text{ Pb, } 10^{-5}$	0	2.4 ± 3.6	1.7 ± 5.6	2.4 ± 3.6	-9.8 ± 8.4
$dz \text{ Pb, } 10^{-5}$	0	-3.3 ± 4.8	2.4 ± 7.7	-3.3 ± 4.8	2.3 ± 11.0
$\sigma^2 \text{ Pb, } \text{\AA}^2$	0.020	0.02008 (5)	0.0209 (1)	0.02009 (5)	0.0184 (1)
$dx \text{ S, } 10^{-4}$	0	1.2 ± 1.7	2.0 ± 2.8	1.2 ± 1.7	13.0 ± 4.2
$dz \text{ S, } 10^{-4}$	0	-1.1 ± 2.3	-1.4 ± 3.6	-1.1 ± 2.3	14.0 ± 5.6
$\sigma^2 \text{ S, } \text{\AA}^2$	0.008	0.0084 (4)	0.0083 (5)	0.0084 (4)	0.0111 (9)
$dx \text{ O(1), } 10^{-4}$	0	-3.2 ± 2.1	-2.9 ± 3.6	-3.2 ± 2.1	41.0 ± 5.0
$dz \text{ O(1), } 10^{-4}$	0	0.0 ± 2.4	0.6 ± 3.8	0.0 ± 2.4	19.0 ± 5.5
$\sigma^2 \text{ O(1), } \text{\AA}^2$	0.025	0.0245 (4)	0.0257 (7)	0.0246 (4)	0.025 (1)
$dx \text{ O(2), } 10^{-4}$	0	1.4 ± 1.9	3.2 ± 3.3	1.4 ± 1.9	$2.7 \pm .47$
$dz \text{ O(2), } 10^{-4}$	0	-3.2 ± 2.5	-2.9 ± 4.2	-3.2 ± 2.6	9.8 ± 6.3
$\sigma^2 \text{ O(2), } \text{\AA}^2$	0.018	0.0185 (4)	0.0192 (7)	0.0185 (4)	0.023 (1)
$dx \text{ O(3), } 10^{-4}$	0	-1.8 ± 1.2	1.3 ± 2.1	1.9 ± 1.2	-0.1 ± 3
$dy \text{ O(3), } 10^{-4}$	0	-1.5 ± 1.8	-2.9 ± 3.0	-1.5 ± 1.8	32.0 ± 4.2
$dz \text{ O(3), } 10^{-4}$	0	-1.0 ± 1.5	-0.9 ± 2.7	-1.0 ± 1.5	-38.0 ± 3.5
$\sigma^2 \text{ O(3), } \text{\AA}^2$	0.015	0.0153 (2)	0.0157 (4)	0.0153 (2)	0.0146 (5)
					0.0149 (6)

Table S3: Estimates of the structural parameters and their uncertainties (± 1 esd) for PbSO_4 obtained by fitting the simulated data containing the multiplicative, additive, and peak-shape systematic errors using both the standard and Bayesian-corrected approaches (see main text).

	True value	ND		XRD		Joint ND and XRD	
		Standard	Bayesian	Standard	Bayesian	Standard	Bayesian
$dx \mathbf{Pb}$	0	-4.5E-04 \pm 3.0E-04	-1.1E-04 \pm 5.4E-04	2.81E-04 \pm 9.5E-05	4E-05 \pm 1.6E-04	1.23E-04 \pm 9.2E-05	1.1E-04 \pm 1.3E-04
$dz \mathbf{Pb}$	0	-3.0E-04 \pm 4.8E-04	-2.5E-04 \pm 9.4E-04	3.6E-04 \pm 1.3E-04	-1E-05 \pm 2.2E-04	9E-05 \pm 1.2E-04	-1.8E-04 \pm 1.7E-04
$\sigma^2 \mathbf{Pb}, \text{\AA}^2$	0.02	1.982E-02 \pm 6.6E-04	1.71E-02 \pm 5.9E-03	1.788E-02 \pm 1.3E-04	1.79E-02 \pm 2.7E-03	1.769E-02 \pm 1.2E-04	1.962E-02 \pm 2.8E-04
$dx \mathbf{S}$	0	-1.19E-03 \pm 7.9E-04	-4E-04 \pm 1.8E-03	5.3E-04 \pm 5.1E-04	-4.3E-04 \pm 8.9E-04	3.2E-04 \pm 4.4E-04	3.3E-04 \pm 6.4E-04
$dz \mathbf{S}$	0	1.17E-02 \pm 1.0E-03	1.1E-03 \pm 2.9E-03	-2.55E-03 \pm 6.8E-04	2E-04 \pm 1.1E-03	2.35E-03 \pm 5.8E-04	9.0E-04 \pm 8.3E-04
$\sigma^2 \mathbf{S}, \text{\AA}^2$	0.008	-3.1E-03 \pm 1.5E-03	4.0E-03 \pm 7.9E-03	6.8E-03 \pm 1.1E-03	5.8E-03 \pm 3.1E-03	6.64E-03 \pm 9.2E-04	8.7E-03 \pm 1.4E-03
$dx \mathbf{O(1)}$	0	3.35E-03 \pm 6.1E-04	-4E-04 \pm 1.2E-03	3.9E-03 \pm 1.2E-03	8E-04 \pm 2.5E-03	3.81E-03 \pm 5.5E-04	-1.59E-03 \pm 7.9E-04
$dz \mathbf{O(1)}$	0	-3.26E-03 \pm 6.5E-04	3E-04 \pm 1.3E-03	4.9E-03 \pm 1.4E-03	-2.7E-04 \pm 2.8E-03	-5.9E-04 \pm 5.9E-04	-1.6E-04 \pm 8.6E-04
$\sigma^2 \mathbf{O(1)}, \text{\AA}^2$	0.025	2.56E-02 \pm 1.2E-03	2.29E-02 \pm 6.0E-03	5E-04 \pm 2.7E-03	2.34E-02 \pm 8.1E-03	2.33E-02 \pm 1.1E-03	2.43E-02 \pm 1.7E-03
$dx \mathbf{O(2)}$	0	9.0E-04 \pm 5.4E-04	0 \pm 1.1E-03	8.9E-03 \pm 1.4E-03	1E-04 \pm 2.5E-03	1.59E-03 \pm 5.3E-04	1.19E-03 \pm 7.4E-04
$dz \mathbf{O(2)}$	0	5.8E-04 \pm 7.3E-04	4E-04 \pm 1.4E-03	8.8E-03 \pm 1.6E-03	-1.5E-03 \pm 3.3E-03	2.78E-03 \pm 6.8E-04	5.3E-04 \pm 9.7E-04
$\sigma^2 \mathbf{O(2)}, \text{\AA}^2$	0.018	1.68E-02 \pm 1.1E-03	1.44E-02 \pm 6.1E-03	1.02E-02 \pm 2.9E-03	1.64E-02 \pm 6.0E-03	1.946E-02 \pm 9.7E-04	1.88E-02 \pm 1.6E-03
$dx \mathbf{O(3)}$	0	1.95E-03 \pm 3.4E-04	0 \pm 7.2E-04	-5.2E-04 \pm 7.4E-04	-3E-04 \pm 1.5E-03	9.0E-04 \pm 3.1E-04	-8.6E-04 \pm 5.1E-04
$dy \mathbf{O(3)}$	0	2.66E-03 \pm 4.8E-04	1E-04 \pm 1.1E-03	3E-04 \pm 1.1E-03	6E-04 \pm 2.5E-03	2.76E-03 \pm 4.4E-04	8.7E-04 \pm 6.8E-04
$dz \mathbf{O(3)}$	0	-5.01E-03 \pm 4.1E-04	5E-04 \pm 1.3E-03	6.5E-03 \pm 1.1E-03	-9E-04 \pm 2.2E-03	-3.23E-03 \pm 3.8E-04	-1.7E-04 \pm 6.2E-04
$\sigma^2 \mathbf{O(3)}, \text{\AA}^2$	0.015	1.159E-02 \pm 5.3E-04	1.20E-02 \pm 6.3E-03	-4.1E-03 \pm 1.7E-03	1.31E-02 \pm 6.1E-03	1.049E-02 \pm 4.6E-04	1.522E-02 \pm 8.9E-04

Table S4: The parameters of the priors and the D-statistics for the different Bayesian models (**M1-M6**) used to fit the experimental data.

	M1	M2	M3	M4	M5	M6
E_μ, ND	0	30	30	30	15	30
E_μ, XRD	0	30	45	45	15	30
k_μ, ND	-	opt	opt	opt	opt	opt
k_μ, XRD	-	opt	opt	opt	opt	opt
E_β, ND	0	30	30	30	15	30
E_β, XRD	0	30	45	45	15	30
k_β, ND	-	opt	opt	opt	opt	opt
k_β, XRD	-	opt	opt	opt	opt	opt
l_δ, ND	0	0.4	0.25	0.4	0.4	0.25
l_δ, XRD	0	0.1	0.045	0.045	0.1	0.045
σ_δ, ND	-	0.1	0.08	0.1	0.1	0.08
σ_δ, XRD	-	0.025	0.015	0.015	0.025	0.015
D-statistics, ND	0.154	0.049	0.030	0.041	0.044	0.0298
D-statistics, XRD	0.182	0.083	0.079	0.080	0.0813	0.0811
Residual wR, ND, %	4.971	3.191	2.59	2.72	2.988	2.583
Residual wR, XRD, %	10.906	7.408	6.991	6.989	7.242	7.043

Table S5: Estimates of the structural parameters and their uncertainties (± 1 esd) for PbSO_4 obtained by fitting the experimental data using various Bayesian models listed in Table S4.

	M1	M2	M3	M4	M5	M6
$dx \text{ Pb}$	1.87E-01 \pm 7.4E-05	1.87E-01 \pm 1.6E-04	1.88E-01 \pm 1.5E-04	1.88E-01 \pm 1.4E-04	1.88E-01 \pm 1.4E-04	1.88E-01 \pm 1.4E-04
$dz \text{ Pb}$	1.67E-01 \pm 1.1E-04	1.67E-01 \pm 2.2E-04	1.67E-01 \pm 2.1E-04	1.67E-01 \pm 2.0E-04	1.67E-01 \pm 2.0E-04	1.67E-01 \pm 2.0E-04
$\sigma^2 \text{ Pb}, \text{\AA}^2$	2.11E-02 \pm 1.1E-04	1.70E-02 \pm 8.0E-04	1.76E-02 \pm 7.2E-04	1.76E-02 \pm 7.2E-04	1.81E-02 \pm 8.1E-04	1.77E-02 \pm 6.9E-04
$dx \text{ S}$	6.52E-02 \pm 2.9E-04	6.48E-02 \pm 6.9E-04	6.45E-02 \pm 6.6E-04	6.41E-02 \pm 6.1E-04	6.48E-02 \pm 6.1E-04	6.48E-02 \pm 6.2E-04
$dz \text{ S}$	6.84E-01 \pm 3.8E-04	6.83E-01 \pm 8.7E-04	6.82E-01 \pm 8.1E-04	6.82E-01 \pm 7.5E-04	6.83E-01 \pm 7.8E-04	6.82E-01 \pm 7.9E-04
$\sigma^2 \text{ S}, \text{\AA}^2$	8.07E-03 \pm 5.4E-04	5.3E-03 \pm 1.5E-03	6.1E-03 \pm 1.4E-03	5.6E-03 \pm 1.3E-03	6.1E-03 \pm 1.4E-03	6.1E-03 \pm 1.3E-03
$dx \text{ O(1)}$	-9.27E-02 \pm 2.1E-04	-9.34E-02 \pm 4.9E-04	-9.05E-02 \pm 4.6E-04	-9.07E-02 \pm 4.1E-04	-9.02E-02 \pm 4.8E-04	-9.04E-02 \pm 4.6E-04
$dz \text{ O(1)}$	5.95E-01 \pm 2.3E-04	5.95E-01 \pm 5.4E-04	5.95E-01 \pm 5.0E-04	5.95E-01 \pm 4.5E-04	5.95E-01 \pm 4.9E-04	5.95E-01 \pm 5.0E-04
$\sigma^2 \text{ O(1)}, \text{\AA}^2$	2.61E-02 \pm 4.4E-04	2.31E-02 \pm 1.5E-03	2.36E-02 \pm 1.4E-03	2.30E-02 \pm 1.2E-03	2.36E-02 \pm 1.4E-03	2.36E-02 \pm 1.3E-03
$dx \text{ O(2)}$	1.94E-01 \pm 2.1E-04	1.94E-01 \pm 4.9E-04	1.92E-01 \pm 4.6E-04	1.93E-01 \pm 4.1E-04	1.92E-01 \pm 4.6E-04	1.92E-01 \pm 4.6E-04
$dz \text{ O(2)}$	5.43E-01 \pm 2.6E-04	5.42E-01 \pm 6.2E-04	5.42E-01 \pm 5.7E-04	5.42E-01 \pm 5.2E-04	5.42E-01 \pm 5.6E-04	5.42E-01 \pm 5.7E-04
$\sigma^2 \text{ O(2)}, \text{\AA}^2$	1.86E-02 \pm 3.8E-04	1.90E-02 \pm 1.5E-03	2.02E-02 \pm 1.4E-03	2.08E-02 \pm 1.3E-03	1.97E-02 \pm 1.5E-03	2.01E-02 \pm 1.4E-03
$dx \text{ O(3)}$	8.09E-02 \pm 1.3E-04	8.11E-02 \pm 3.1E-04	8.08E-02 \pm 2.9E-04	8.08E-02 \pm 2.6E-04	8.06E-02 \pm 2.9E-04	8.08E-02 \pm 2.9E-04
$dy \text{ O(3)}$	2.70E-02 \pm 1.8E-04	2.76E-02 \pm 4.6E-04	2.89E-02 \pm 4.3E-04	2.87E-02 \pm 3.8E-04	2.79E-02 \pm 4.0E-04	2.88E-02 \pm 4.3E-04
$dz \text{ O(3)}$	8.09E-01 \pm 1.6E-04	8.09E-01 \pm 4.9E-04	8.08E-01 \pm 4.7E-04	8.09E-01 \pm 4.1E-04	8.08E-01 \pm 4.2E-04	8.08E-01 \pm 4.7E-04
$\sigma^2 \text{ O(3)}, \text{\AA}^2$	1.82E-02 \pm 2.3E-04	1.55E-02 \pm 1.1E-03	1.71E-02 \pm 1.0E-03	1.65E-02 \pm 9.7E-04	1.76E-02 \pm 1.1E-03	1.70E-02 \pm 1.0E-03

Uncertainty estimation for structural parameters

Let us denote

$$\psi(\boldsymbol{a}) \equiv -\ln(p(\mathbf{y}_{exp} | \boldsymbol{a}, I, I_{sys})) = \frac{1}{2} \Delta \mathbf{y}_a^T \boldsymbol{\Sigma}_{p,\gamma}^{-1} \Delta \mathbf{y}_a.$$

We approximate $\psi(\boldsymbol{a})$ by expanding it to second order in \boldsymbol{a} around its minimum value at \boldsymbol{a}_0

$$\psi(\boldsymbol{a}) \approx \psi(\boldsymbol{a}_0) + \frac{1}{2} (\boldsymbol{a} - \boldsymbol{a}_0)^T H_\psi (\boldsymbol{a} - \boldsymbol{a}_0),$$

The covariance matrix for estimated parameters is therefore $\langle \Delta \boldsymbol{a} \Delta \boldsymbol{a}^T \rangle = H_\psi^{-1}$, where H_ψ is the Hessian matrix $H_\psi = \nabla_{\boldsymbol{a}} \nabla_{\boldsymbol{a}}^T \psi|_{\boldsymbol{a}_0}$.

H_ψ can be obtained by differentiation of the previous equation

$$H_\psi^{-1} = J_y^T \boldsymbol{\Sigma}_{p,\gamma}^{-1} J_y + H_y \boldsymbol{\Sigma}_{p,\gamma}^{-1} \Delta \mathbf{y}_a,$$

where J_y and H_y are the Jacobian and Hessian matrices for \mathbf{y}_a , respectively. Neglecting the quadratic terms, we obtain

$$H_\psi^{-1} \approx J_y^T \boldsymbol{\Sigma}_{p,\gamma}^{-1} J_y.$$

Derivation of equation (29) (main text)

According to equation (15) (main text), the covariance matrix for the peak-shape corrections can be evaluated as

$$\boldsymbol{\Sigma}_{p,\delta}^{-1} = \boldsymbol{\Sigma}_p^{-1} - \boldsymbol{\Sigma}_p^{-1/2} \boldsymbol{\Sigma}_y^{-1/2} \mathbf{M}_\delta^{-1} \boldsymbol{\Sigma}_y^{-1/2} \boldsymbol{\Sigma}_p^{-1/2}.$$

Combining (15) with equation (16) (main text) yields

$$\boldsymbol{\Sigma}_{p,\delta}^{-1} = \boldsymbol{\Sigma}_p^{-1} - \boldsymbol{\Sigma}_p^{-1/2} \boldsymbol{\Sigma}_y^{-1/2} [\boldsymbol{\Sigma}_y^{-1} + \boldsymbol{\Sigma}_\delta^{-1}]^{-1} \boldsymbol{\Sigma}_y^{-1/2} \boldsymbol{\Sigma}_p^{-1/2}.$$

This equation can be transformed to

$$\boldsymbol{\Sigma}_{p,\delta}^{-1} = \boldsymbol{\Sigma}_p^{-1/2} \left(I - \boldsymbol{\Sigma}_y^{-1/2} [\boldsymbol{\Sigma}_y^{-1} + \boldsymbol{\Sigma}_\delta^{-1}]^{-1} \boldsymbol{\Sigma}_y^{-1/2} \right) \boldsymbol{\Sigma}_p^{-1/2}$$

and

$$\boldsymbol{\Sigma}_{p,\delta}^{-1} = \boldsymbol{\Sigma}_p^{-1/2} \left(\mathbf{I} - \left[\mathbf{I} + \left(\boldsymbol{\Sigma}_y^{-1/2} \boldsymbol{\Sigma}_\delta \boldsymbol{\Sigma}_y^{-1/2} \right)^{-1} \right]^{-1} \right) \boldsymbol{\Sigma}_p^{-1/2}.$$

Recalling that $\boldsymbol{\Sigma}_y^{-1/2} \boldsymbol{\Sigma}_\delta \boldsymbol{\Sigma}_y^{-1/2} = \mathbf{K}$, we obtain

$$\boldsymbol{\Sigma}_{p,\delta}^{-1} = \boldsymbol{\Sigma}_p^{-1/2} (\mathbf{I} - [\mathbf{I} + \mathbf{K}^{-1}]^{-1}) \boldsymbol{\Sigma}_p^{-1/2}.$$

To avoid inversion of the possibly ill-conditioned matrix \mathbf{K} , we rearrange the operations as

$$\boldsymbol{\Sigma}_{p,\delta}^{-1} = \boldsymbol{\Sigma}_p^{-1/2} (\mathbf{I} - \mathbf{K}[\mathbf{I} + \mathbf{K}]^{-1}) \boldsymbol{\Sigma}_p^{-1/2}.$$