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Supporting information for article:

Multivariate versus traditional quantitative phase analysis of X-ray powder diffraction and fluorescence data of mixtures showing preferred orientation and microabsorption

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Multivariate vs. traditional quantitative phase analysis of
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X-ray Powder Diffraction; Quantitative phase analysis; Rietveld refinement; Multivariate analysis; Principal

Component Analysis

SUPPLEMENTARY MATERIAL

1. Supplementary figures

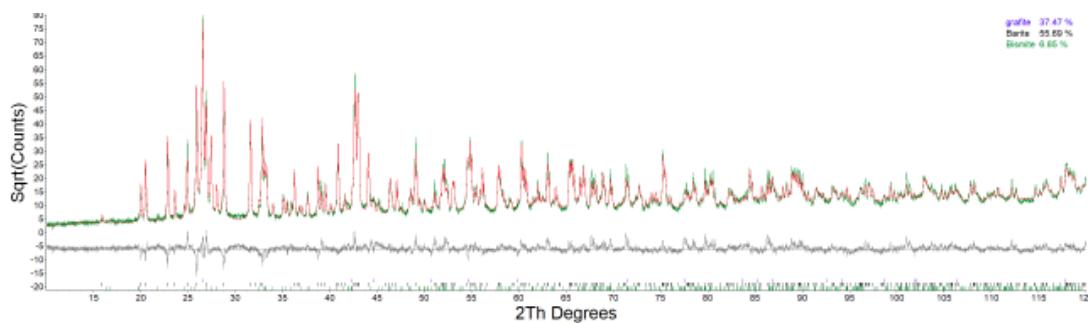


Figure S1: Whole profile fitting performed using Rietveld refinement on sample SA1 from dataset D1. The calculation of the residuals does not suggest that some parameters in the fit model have been neglected.

SUPPLEMENTARY MATERIAL

2. Quantification tables

Table S1: Results of the supervised analysis performed by multivariate approach.

Dataset D1 - XRPD			
Phase	Supervised multiple regression analysis		
	SA 1	SA 2	SA 3
Ba	0.634 (-0.032)	0.236 (0.069)	0.134 (-0.033)
Bi	0.216 (0.049)	0.577 (-0.089)	0.252 (0.085)
Gr	0.150 (-0.017)	0.188 (0.021)	0.615 (-0.051)

Dataset D2 - XRPD			
Phase	Supervised multiple regression analysis		
	SA 1	SA 2	SA 3
Ba	0.615 (-0.051)	0.143 (-0.024)	0.077 (-0.089)
Bi	0.137 (-0.030)	0.655 (-0.011)	0.244 (0.077)
Gr	0.248 (0.081)	0.202 (0.035)	0.678 (0.012)

Dataset D3 - XRPD			
Phase	Supervised multiple regression analysis		
	SA 1	SA 2	SA 3
Ba	0.608 (-0.058)	0.166 (-0.001)	0.192 (0.025)
Bi	0.156 (-0.011)	0.580 (-0.086)	0.169 (0.002)
Zn	0.236 (0.069)	0.254 (0.087)	0.638 (-0.028)

Dataset D4 - XRPD			
Phase	Supervised multiple regression analysis		
	SA 1	SA 2	SA 3
Ba	0.612 (-0.054)	0.209 (0.042)	0.213 (0.046)
Bi	0.183 (0.016)	0.605 (-0.061)	0.216 (0.049)
Ur	0.204 (0.037)	0.185 (0.018)	0.570 (-0.096)

SUPPLEMENTARY MATERIAL

Table S2: Results of the unsupervised analysis performed by multivariate approach.

Dataset D1 - XRPD							
Phase		Unsupervised multiple regression analysis					
	S4 (Ba Bi)	S5 (Ba Gr)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.582 (0.082)	0.367 (-0.133)	0.000 (0.000)	0.374 (0.041)	0.634 (-0.032)	0.235 (0.068)	0.133 (-0.034)
Bi	0.418 (-0.083)	0.014 (0.014)	0.581 (0.081)	0.354 (0.021)	0.215 (0.048)	0.577 (-0.089)	0.257 (0.090)
Gr	0.000 (0.000)	0.618 (0.118)	0.419 (-0.081)	0.271 (-0.062)	0.150 (-0.017)	0.188 (-0.017)	0.610 (-0.056)

Dataset D2 - XRPD							
Phase		Unsupervised multiple regression analysis					
	S4 (Ba Bi)	S5 (Ba Gr)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.582 (0.082)	0.436 (-0.064)	0.000 (0.000)	0.246 (-0.087)	0.615 (-0.051)	0.143 (-0.024)	0.077 (-0.090)
Bi	0.418 (-0.082)	0.000 (0.000)	0.580 (0.080)	0.390 (0.057)	0.137 (-0.030)	0.655 (-0.011)	0.244 (0.077)
Gr	0.000 (0.000)	0.564 (0.064)	0.419 (-0.081)	0.363 (0.030)	0.248 (0.081)	0.202 (0.035)	0.678 (0.012)

Dataset D3 - XRPD							
Phase		Unsupervised multiple regression analysis					
	S4 (Ba Bi)	S5 (Ba Zn)	S6 (Bi Zn)	S7 (Ba Bi Zn)	SA 1	SA 2	SA 3
Ba	0.562 (0.062)	0.381 (-0.119)	0.000 (0.000)	0.385 (0.052)	0.608 (-0.058)	0.166 (-0.001)	0.192 (0.025)
Bi	0.438 (-0.062)	0.000 (0.000)	0.444 (-0.056)	0.246 (-0.054)	0.156 (-0.011)	0.580 (-0.086)	0.169 (0.002)
Gr	0.000 (0.000)	0.619 (0.119)	0.555 (0.055)	0.368 (0.035)	0.236 (0.069)	0.254 (0.087)	0.638 (-0.028)

Dataset D4 - XRPD							
Phase		Unsupervised multiple regression analysis					
	S4 (Ba Bi)	S5 (Ba Ur)	S6 (Bi Ur)	S7 (Ba Bi Ur)	SA 1	SA 2	SA 3
Ba	0.545 (0.045)	0.587 (0.087)	0.000 (0.000)	0.333 (0.000)	0.607 (-0.059)	0.209 (0.042)	0.216 (0.049)
Bi	0.426 (-0.074)	0.013 (0.013)	0.376 (-0.124)	0.382 (0.049)	0.180 (0.013)	0.601 (-0.065)	0.213 (0.046)
Gr	0.028 (0.028)	0.399 (-0.101)	0.624 (0.124)	0.284 (-0.049)	0.213 (0.046)	0.189 (0.022)	0.571 (-0.096)

Table S3: Results of the blind analysis performed by multivariate approach.

Dataset D1 - XRPD										
Phase		Blind analysis								
	S1 (Ba)	S2 (Bi)	S3 (Gr)	S4 (Ba Bi)	S5 (Ba Gr)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.995 (-0.005)	-0.027 (-0.027)	-0.011 (-0.011)	0.366 (-0.134)	0.563 (0.063)	-0.031 (-0.031)	0.384 (0.051)	0.748 (0.081)	0.133 (-0.034)	0.255 (0.088)
Bi	0.005 (0.005)	1.000 (0.000)	0.012 (0.012)	0.575 (0.075)	0.016 (0.016)	0.384 (-0.116)	0.232 (-0.101)	0.000 (-0.167)	0.575 (-0.091)	0.111 (-0.056)
Gr	0.000 (0.000)	0.027 (0.000)	1.000 (0.000)	0.059 (0.059)	0.421 (-0.079)	0.647 (0.147)	0.384 (0.051)	0.252 (0.085)	0.292 (0.125)	0.634 (-0.032)

Dataset D2 - XRPD										
Phase		Blind analysis								
	S1 (Ba)	S2 (Bi)	S3 (Gr)	S4 (Ba Bi)	S5 (Ba Gr)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	1.000 (0.000)	-0.065 (-0.065)	-0.074 (-0.074)	0.621 (0.121)	0.382 (-0.118)	-0.042 (-0.042)	0.376 (0.043)	0.695 (0.029)	0.218 (0.051)	0.090 (-0.077)
Bi	0.000 (0.000)	1.000 (0.000)	0.074 (0.074)	0.368 (-0.132)	0.046 (0.046)	0.546 (0.046)	0.343 (0.010)	0.137 (-0.030)	0.645 (-0.021)	0.233 (-0.100)
Gr	0.000 (0.000)	0.065 (0.000)	1.000 (0.000)	0.011 (0.011)	0.572 (0.072)	0.496 (0.004)	0.281 (-0.115)	0.168 (0.001)	0.137 (-0.030)	0.677 (0.011)

Dataset D3 - XRPD										
Phase		Blind analysis								
	S1 (Ba)	S2 (Bi)	S3 (Zn)	S4 (Ba Bi)	S5 (Ba Zn)	S6 (Bi Zn)	S7 (Ba Bi Zn)	SA 1	SA 2	SA 3
Ba	0.847 (-0.153)	-0.087 (-0.087)	0.000 (0.000)	0.468 (0.032)	0.432 (0.068)	-0.050 (-0.050)	0.246 (0.087)	0.500 (-0.166)	0.167 (0.000)	0.111 (-0.056)
Bi	0.000 (0.000)	0.087 (0.087)	1.000 (0.000)	0.445 (-0.055)	0.029 (0.029)	0.482 (-0.018)	0.290 (-0.043)	0.202 (0.035)	0.610 (-0.056)	0.229 (0.062)
Zn	0.153 (0.153)	1.000 (0.000)	0.000 (0.000)	0.087 (0.000)	0.540 (0.040)	0.569 (0.069)	0.465 (0.132)	0.300 (0.133)	0.223 (0.056)	0.660 (-0.006)

Dataset D4 - XRPD										
Phase		Blind analysis								
	S1 (Ba)	S2 (Bi)	S3 (Ur)	S4 (Ba Bi)	S5 (Ba Ur)	S6 (Bi Ur)	S7 (Ba Bi Ur)	SA 1	SA 2	SA 3
Ba	0.954 (-0.046)	0.000 (0.000)	0.000 (0.000)	0.453 (-0.047)	0.236 (-0.214)	0.003 (0.003)	0.181 (-0.152)	0.408 (-0.254)	0.091 (0.076)	0.028 (-0.139)
Bi	0.006 (0.006)	0.001 (0.001)	1.000 (0.000)	0.464 (0.036)	0.000 (0.000)	0.429 (0.071)	0.365 (0.032)	0.232 (0.065)	0.667 (0.001)	0.190 (0.023)
Ur	0.040 (0.040)	1.000 (0.000)	0.000 (0.000)	0.084 (0.084)	0.764 (0.264)	0.569 (0.069)	0.454 (0.121)	0.360 (0.193)	0.242 (0.075)	0.783 (0.117)

SUPPLEMENTARY MATERIAL

Table S4: Results of the quantitative phase analysis performed by Rietveld refinement.

Dataset D1 - XRPD							
Phase	Rietveld refinement						
	S4 (Ba Bi)	S5 (Ba Gr)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.139 (-0.361)	0.000 (0.000)	0.293 (-0.040)	0.556 (-0.110)	0.207 (0.040)	0.044 (-0.123)
Bi	0.233 (-0.267)	0.000 (0.000)	0.189 (-0.311)	0.140 (-0.193)	0.069 (-0.098)	0.336 (-0.330)	0.037 (-0.130)
Gr	0.000 (0.000)	0.861 (0.361)	0.811 (0.311)	0.567 (0.234)	0.375 (0.208)	0.457 (0.290)	0.919 (0.253)

Dataset D2 - XRPD							
Phase	Rietveld refinement						
	S4 (Ba Bi)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3	
Ba	0.767 (0.267)	0.153 (-0.347)	0.000 (0.000)	0.175 (-0.158)	0.491 (-0.175)	0.108 (0.013)	0.029 (-0.138)
Bi	0.233 (-0.267)	0.000 (0.000)	0.188 (-0.312)	0.150 (-0.183)	0.079 (-0.088)	0.383 (-0.283)	0.044 (-0.123)
Gr	0.000 (0.000)	0.847 (0.347)	0.812 (0.312)	0.675 (0.342)	0.430 (0.263)	0.509 (0.342)	0.927 (0.261)

Dataset D3 - XRPD							
Phase	Rietveld refinement						
	S4 (Ba Bi)	S6 (Bi Zn)	S7 (Ba Bi Zn)	SA 1	SA 2	SA 3	
Ba	0.767 (0.267)	0.377 (-0.123)	0.000 (0.000)	0.430 (0.097)	0.654 (-0.012)	0.238 (0.071)	0.175 (0.008)
Bi	0.233 (-0.267)	0.000 (0.000)	0.200 (-0.300)	0.122 (-0.211)	0.064 (-0.103)	0.342 (-0.324)	0.061 (-0.106)
Zn	0.000 (0.000)	0.623 (0.123)	0.800 (0.000)	0.448 (0.115)	0.282 (0.115)	0.420 (0.253)	0.764 (0.098)

Dataset D4 - XRPD							
Phase	Rietveld refinement						
	S4 (Ba Bi)	S6 (Bi Ur)	S7 (Ba Bi Ur)	SA 1	SA 2	SA 3	
Ba	0.767 (0.267)	0.471 (-0.129)	0.000 (0.000)	0.525 (0.192)	0.749 (0.083)	0.263 (0.096)	0.190 (0.023)
Bi	0.233 (-0.267)	0.000 (0.000)	0.149 (-0.351)	0.168 (-0.165)	0.075 (-0.092)	0.322 (-0.344)	0.058 (-0.109)
Ur	0.000 (0.000)	0.529 (0.129)	0.851 (0.351)	0.308 (-0.025)	0.176 (0.009)	0.415 (0.248)	0.752 (0.086)

SUPPLEMENTARY MATERIAL

Table S5: Results of the quantitative phase analysis performed by single PONKCS approach.

Dataset D1 - XRPD						
Phase						
Single PONKCS on barite						
	S4 (Ba Bi)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.000 (0.000)	0.542 (0.209)	0.760 (0.094)	0.300 (0.133)	0.171 (0.004)
Bi	0.233 (-0.267)	0.522 (0.022)	0.243 (-0.090)	0.091 (-0.076)	0.448 (-0.218)	0.132 (-0.035)
Gr	0.000 (0.000)	0.478 (-0.022)	0.215 (-0.118)	0.149 (-0.018)	0.252 (0.085)	0.698 (0.032)
Phase						
Single PONKCS on bismite						
	S4 (Ba Bi)	S5 (Ba Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.517 (0.017)	0.489 (0.156)	0.722 (0.056)	0.266 (0.099)	0.133 (-0.034)
Bi	0.233 (-0.267)	0.000 (0.000)	0.252 (-0.081)	0.099 (-0.068)	0.439 (-0.222)	0.128 (-0.039)
Gr	0.000 (0.000)	0.483 (-0.017)	0.259 (-0.074)	0.179 (0.012)	0.294 (0.127)	0.739 (0.073)

Dataset D2 - XRPD						
Phase						
Single PONKCS on barite						
	S4 (Ba Bi)	S6 (Bi Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.000 (0.000)	0.416 (0.083)	0.606 (-0.060)	0.191 (0.024)	0.098 (-0.069)
Bi	0.233 (-0.267)	0.454 (-0.046)	0.288 (-0.045)	0.088 (-0.079)	0.546 (-0.120)	0.119 (-0.048)
Gr	0.000 (0.000)	0.546 (0.046)	0.296 (-0.037)	0.306 (0.139)	0.263 (0.096)	0.793 (0.127)
Phase						
Single PONKCS on bismite						
	S4 (Ba Bi)	S5 (Ba Gr)	S7 (Ba Bi Gr)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.557 (0.057)	0.442 (0.109)	0.608 (-0.058)	0.198 (0.031)	0.108 (-0.059)
Bi	0.233 (-0.267)	0.000 (0.000)	0.306 (-0.027)	0.087 (-0.080)	0.573 (-0.093)	0.131 (-0.036)
Gr	0.000 (0.000)	0.443 (-0.057)	0.253 (-0.080)	0.305 (0.138)	0.229 (0.062)	0.761 (0.095)

Dataset D3 - XRPD						
Phase						
Single PONKCS on barite						
	S4 (Ba Bi)	S6 (Bi Zn)	S7 (Ba Bi Zn)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.000 (0.000)	0.558 (-0.108)	0.706 (0.040)	0.281 (0.114)	0.240 (0.037)
Bi	0.233 (-0.267)	0.482 (-0.018)	0.156 (-0.177)	0.073 (-0.094)	0.417 (-0.249)	0.092 (-0.075)
Zn	0.000 (0.000)	0.518 (0.018)	0.286 (-0.047)	0.221 (0.054)	0.302 (0.135)	0.668 (0.002)
Phase						
Single PONKCS on bismite						
	S4 (Ba Bi)	S5 (Ba Zn)	S7 (Ba Bi Zn)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.654 (0.154)	0.626 (0.293)	0.800 (0.134)	0.343 (0.176)	0.382 (0.215)
Bi	0.233 (-0.267)	0.000 (0.000)	0.159 (-0.174)	0.070 (-0.097)	0.444 (-0.222)	0.095 (-0.072)
Zn	0.000 (0.000)	0.346 (-0.154)	0.215 (-0.118)	0.130 (-0.037)	0.213 (0.046)	0.523 (-0.143)

Dataset D4 - XRPD						
Phase						
Single PONKCS on barite						
	S4 (Ba Bi)	S6 (Bi Ur)	S7 (Ba Bi Ur)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.000 (0.000)	0.617 (0.284)	0.831 (0.165)	0.312 (0.145)	0.262 (0.095)
Bi	0.233 (-0.267)	0.169 (-0.331)	0.185 (-0.148)	0.073 (-0.094)	0.371 (-0.295)	0.080 (-0.087)
Ur	0.000 (0.000)	0.831 (0.331)	0.199 (-0.134)	0.096 (-0.071)	0.317 (0.150)	0.658 (-0.008)
Phase						
Single PONKCS on bismite						
	S4 (Ba Bi)	S5 (Ba Ur)	S7 (Ba Bi Ur)	SA 1	SA 2	SA 3
Ba	0.767 (0.267)	0.898 (0.398)	0.738 (0.405)	0.904 (0.238)	0.427 (0.260)	0.598 (0.431)
Bi	0.233 (-0.267)	0.000 (0.000)	0.223 (-0.110)	0.081 (-0.086)	0.513 (-0.153)	0.174 (0.007)
Ur	0.000 (0.000)	0.102 (-0.398)	0.040 (-0.293)	0.015 (-0.152)	0.060 (-0.107)	0.228 (-0.438)

SUPPLEMENTARY MATERIAL

Table S6: Results of the quantification analyses performed on XRPD data sets. On the left, quantification was made by double PONKCS on barite. On the right, double PONKCS on bismite was used.

Dataset D1 - XRPD						
Phase	Double PONKCS on barite			Double PONKCS on bismite		
	SA 1	SA 2	SA 3	SA 1	SA 2	SA 3
Ba	0.536 (-0.130)	0.140 (-0.027)	0.105 (-0.017)	0.493 (-0.173)	0.200 (0.033)	0.206 (0.039)
Bi	0.147 (-0.020)	0.507 (-0.159)	0.181 (0.014)	0.146 (-0.021)	0.477 (-0.189)	0.130 (-0.037)
Gr	0.317 (0.150)	0.353 (0.186)	0.715 (0.049)	0.361 (0.194)	0.323 (0.156)	0.665 (-0.001)

Dataset D2 - XRPD						
Phase	Double PONKCS on barite			Double PONKCS on bismite		
	SA 1	SA 2	SA 3	SA 1	SA 2	SA 3
Ba	0.512 (-0.154)	0.139 (-0.028)	0.118 (-0.049)	0.434 (-0.232)	0.151 (-0.016)	0.135 (-0.032)
Bi	0.098 (-0.069)	0.563 (-0.103)	0.186 (0.019)	0.083 (-0.084)	0.591 (-0.075)	0.155 (-0.012)
Gr	0.391 (0.224)	0.298 (0.0131)	0.696 (0.030)	0.484 (0.317)	0.258 (0.091)	0.710 (0.044)

Dataset D3 - XRPD						
Phase	Double PONKCS on barite			Double PONKCS on bismite		
	SA 1	SA 2	SA 3	SA 1	SA 2	SA 3
Ba	0.504 (-0.162)	0.120 (-0.047)	0.131 (-0.036)	0.533 (-0.133)	0.118 (-0.049)	0.148 (-0.019)
Bi	0.191 (0.024)	0.611 (-0.055)	0.174 (0.007)	0.185 (0.018)	0.662 (-0.004)	0.193 (0.026)
Zn	0.306 (0.139)	0.269 (0.102)	0.696 (0.030)	0.283 (0.116)	0.220 (0.053)	0.659 (-0.007)

Dataset D4 - XRPD						
Phase	Double PONKCS on barite			Double PONKCS on bismite		
	SA 1	SA 2	SA 3	SA 1	SA 2	SA 3
Ba	0.593 (-0.073)	0.116 (-0.051)	0.126 (-0.041)	0.582 (-0.084)	0.135 (-0.032)	0.135 (-0.032)
Bi	0.197 (-0.030)	0.432 (-0.234)	0.108 (0.059)	0.170 (0.003)	0.518 (-0.148)	0.125 (-0.042)
Ur	0.209 (0.042)	0.450 (0.283)	0.765 (0.099)	0.248 (0.081)	0.347 (0.180)	0.740 (0.074)

Table S7: Results of the quantification analyses performed on XRF data set D3. On the left, quantification was made by fundamental parameters approach. On the right, supervised multiple regression analysis was used.

Dataset D3 - XRF						
Phase	FP			SMRA		
	SA 1	SA 2	SA 3	SA 1	SA 2	SA 3
Ba	0.523 (-0.143)	0.144 (-0.023)	0.332 (0.165)	0.623 (-0.043)	0.214 (0.047)	0.163 (-0.004)
Bi	0.152 (-0.015)	0.668 (0.002)	0.179 (0.012)	0.158 (-0.009)	0.553 (-0.113)	0.093 (-0.074)
Zn	0.129 (-0.038)	0.165 (-0.002)	0.706 (-0.04)	0.280 (0.113)	0.216 (0.049)	0.504 (-0.162)