

Quality Assessment of the CL-20/HMX Cocrystal Utilising Digital Image Processing

Dirk Herrmannsdörfer^{*,[a]} and Thomas M. Klapötke^[b]

Abstract: The reduction of liquid and gas inclusions in the crystals is an effective strategy for the production of reduced sensitivity high explosives. Assessment of the achieved crystal quality is paramount for the improvement of the crystallisation techniques. Here we present the quality evaluation of the CL-20/HMX cocrystal obtained from semi-batch reaction cocrystallisation (SBRC), batch reaction cocrystallization (BRC), and antisolvent crystallisation by comparison of the results of digital image processing of photomicrographs of crystals immersed in an optically

equally dense liquid, ¹H NMR, HPLC, GC, helium pycnometry, SEM, pXRD, and DSC. It was found that digital image processing is capable of differentiation between crystal qualities of batches that are indistinguishable by all the other listed methods. It presents itself as a very promising tool for crystal quality assessment and improvement. The analysis shows that SBRC can produce coarse crystals of the same quality on a pilot plant scale as antisolvent crystallisation on a laboratory scale.

Keywords: CL-20 • HMX • cocrystal • quality • image processing

1 Introduction

Reducing the sensitivity of high explosives to improve the safety of storage under combat and non-combat conditions is of special interest in energetic materials research [1]. Many factors, such as surface roughness [2], morphology [3], chemical purity [4], crystallinity [5], and internal defects [6] have been linked to the sensitivity of high explosives. Internal defects and dislocations, often caused by solvent or gas inclusions, play a major role in determining the sensitivity of the explosive [7]. Because of the density difference between solvent, gas, and explosive, skeletal density could be used as an indirect method to quantify internal defects [7,8] and was used to determine differences in shock response of the explosives dependent on the measured density [7,9]. Another, more direct, way of defect analysis is photomicrography of the particles immersed in a liquid of matching refractive index [2,4,8,10]. This procedure reduces surface diffraction on the crystals and, thereby, highlights internal defects. In the past, this method, however, has only been used as a quantitative indicator by Kim *et al.* [11] by manually defining the crystal boundaries. Now that Lins, Heisel, and Wohlgemuth have developed an algorithm that enables one to automate the detection of crystals and the quantification of the internal defects highlighted by optical immersion [12], this method can be utilised for quantitative differentiation between batches of different crystal quality far more conveniently. Recently, SBRC a novel crystallisation technique for the scaled-up production of the CL-20/HMX cocrystal has been presented [13]. It promises to combine the crystal quality obtained from antisolvent crystallisation [14] with the efficiency of BRC. To put the ob-

tained crystal quality of SBRC in perspective, here we apply image processing together with a variety of conventional analysis methods to compare the crystal quality obtainable from SBRC with antisolvent crystallisation and BRC.

2 Experimental Section

ε-CL-20 (lot number 573S98) was obtained from SNPE. The chemical purity has been determined via ¹H NMR and HPLC to be 98.3 and 99.4%, respectively. Fine β-HMX (lot number

[a] D. Herrmannsdörfer
Energetic Materials
Fraunhofer Institute for Chemical Technology ICT
Joseph-von-Fraunhofer-Str. 7
76327 Pfinztal, Germany
Fax: (+)49 (721) 4640-111
*e-mail: dirk.herrmannsdorfer@ict.fraunhofer.de

[b] T. M. Klapötke
Department of Chemistry
Energetic Materials Research
Ludwig-Maximilians University of Munich
Butenandtstr. 5-13 (Haus D)
81377 Munich, Germany

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NSI 00E 000 E004) was purchased from Chemring Nobel. The chemical purity has been determined via ^1H NMR and HPLC to be 98.7 and 99.3%, respectively. Coarse β -HMX (NSO131, lot number 20173558) was purchased from Eurochem. The chemical purity has been determined via ^1H NMR and HPLC to be 99.4 and 99.9%, respectively. Acetonitrile (ACN) (HPLC grade) was purchased from Carl Roth GmbH, stored over 3 Å molecular sieve, and used as received.

For antisolvent crystallisation, 3000 mg ACN (73.08 mmol) was added to 152 mg fine HMX (0.51 mmol) and 1472 mg CL 20 (3.36 mmol) in 20 mL glass vessels. The solid was dissolved at 343.15 K and 800 rpm for 10 minutes. Subsequently, the solution was cooled to 333.15 K. The seed crystal suspension was added, and the reaction vessels were air tightly connected to the pump tube via teflon fittings. 2000 mg 2-propanol (33.27 mmol) was dispensed over the course of 16.6 h using a Hirschmann ROTARUS VOLUME 501 metering pump equipped with a ROTARUS MKF 12–8 12 channel pump head. During crystallisation, the temperature was kept constant at 333.15 K, and the vessels were agitated at 600 rpm. The solid phase was washed according to the standard washing procedure [14]. Five batches carried out in parallel were mixed to obtain about 1 g of cocrystal.

For BRC, 80.0 g (1.95 mol) ACN was added to 28.0 g coarse HMX (94.5 mmol) and 112.0 g (255.6 mmol) CL 20 in a 250 mL jacketed flask with a rounded bottom. The slurry was agitated at 240 rpm for 2 h at 333.15 K via an overhead stirrer equipped with a paddle stirrer. The stirrer's contour closely matches the inner wall contour of the jacketed vessel. After 2 h, the stirrer was removed and the slurry was transferred into a Büchner funnel using a BRAUN omnifix 100 mL syringe without a cannula attached to avoid clogging. After the removal of the mother liquor, the product crystals were washed with 30 mL 1:1 2-propanol:ACN, 30 mL 2-propanol:ACN (8:2), 30 mL 2-propanol:ACN (9:1), 30 mL 2-propanol (two times), and 100 mL 2-propanol (once) to ensure the total removal of the mother liquor.

For SBRC, 122 g (2.97 mol) ACN was added to 52.95 g CL-20 (120.8 mmol) and 5.35 g coarse HMX (18.1 mmol) in a 250 mL flat bottomed jacketed flask that was temperature controlled to 333.15 K using a Lauda RC6 CP thermostat. The reaction mixture was agitated by a specially designed captured magnetic stir bar that was propelled via a heidolph MR Hei-End magnetic stirrer set to 250 rpm. After complete dissolution and thermal equilibration, the seed crystals were added to the solution. The concentration was adjusted to ensure about 10% seed crystal dissolution to reduce surface defects that would reduce the crystal quality. After equilibrium was reached, the solid dosing of a mixture of 90 g CL-20 (205 mmol), 25 g coarse HMX (84 mmol), and 5 g fine HMX (17 mmol) was started. The solid was dispensed by a LAMBDA Instruments GmbH DOSER 0.2 L. A slow stream of pressurised air was vented through the solid doser to prevent cementation of the solid due to ACN vapours. 1 h after all solid was dispensed, the

stirrer was removed and the slurry transferred into a Büchner funnel using a BRAUN omnifix 100 mL syringe without a cannula attached to avoid clogging. The mother liquor was removed, and the product crystals were washed with 30 mL 2-propanol:ACN (8:2), 30 mL 2-propanol:ACN (9:1), and five times with 20 mL 2-propanol to ensure the total removal of the mother liquor. The crystals were dried under ambient conditions. For SBRC1 and 2, a sieve fraction of $D(4,3) = 76\text{ }\mu\text{m}$ of a failed SBRC experiment was used as seed crystals. For SBRC3 and 4, a sieve fraction $D(4,3) = 132\text{ }\mu\text{m}$ of two mixed failed SBRC batches was used as seed crystals. The two failed batches were also seeded with the same seed crystals as SBRC1 and 2. The crystals of SBRC1 and 2 were, therefore, grown in three steps and the crystals of SBRC3 and 4 are the product of four consecutive growth processes. The crystallisation time for SBRC1, 2, 3 and 4 was 26 h, 26.5 h, 24 h, and 20 h, respectively.

DSC analysis was carried out using a TA Instruments DSC Q2000 V24.10 build 122. Samples were heated from 298 up to 543 K at the rate of 1 K min^{-1} in a hermetically sealed aluminium pan. The sample quantity in all experiments was between 0.5 and 1.5 mg.

The bulk density was determined using a micromeritics AccuPyc 1340 TEC 10 cm^3 with He 5.0 as measurement gas. The equilibration pressure change was set to the standard $0.345\text{ hPa min}^{-1}$. The heating/cooling element was set to 292.95 K for all measurements to achieve an average chamber temperature close to 293.15 K. A calibration of the chamber volumes was carried out before the series of measurements. About 10 g material was weight in using a Kern 770 analytical balance (accuracy 0.1 mg). 300 flushing cycles ensured total sample dryness during the measurement. Between 50 and 300 data points were collected for each measurement. At least two true repeat measurements were carried out for each sample. Because only 1 g of A1 was available, this density measurement was carried out in the 1 cm^3 measurement cell. It was shown that the required precision needed to compare the batches can only be achieved under repeat measurement conditions in the same sample cell [15]. The offset between the two cells was determined by measuring SBRC3 three times also in the 1 cm^3 cell, and the obtained density value for A1 was adjusted accordingly.

For solvent inclusion determination, about 50 mg samples were dissolved in dry dimethylformamide. $1\text{ }\mu\text{m}$ solution was injected into the Agilent 6890N GC-FID equipped with a DB-624 $60\text{ m} \times 0.25\text{ mm ID} \times 1.4\text{ }\mu\text{m}$ film column. The split ratio was 10 and the injection port temperature 503 K. The helium flow was 2 mL min^{-1} and the column was kept at 323 K for 4 min, then heated up to 353 K with a heating rate of 5 K min^{-1} . From 353 K up to 533 K, the heating rate was 20 K min^{-1} . The detector temperature was 553 K.

Particle diameters were determined with a Malvern Mastersizer 2000 version 5.60 in 2-propanol as dispersion medium. The agitation speed was 2450 rpm. 1.69 was chosen as the refractive index, and the absorption coefficient was

selected individually to obtain the best results. Three measurements each consisting of 10000 individual scans were averaged.

X-ray powder diffraction measurements were performed on a D8 Advance from Bruker AXS equipped with a copper tube, two 2.5° Soller collimators, an anti-scatter screen, a flip stick stage, and a silicon strip detector (LynxEye). Samples were milled to a particle diameter of less than 10 µm. The reflection range was scanned in 0.01° 2θ steps from 10–42° 2θ. Each measurement was accumulated for 20 s. The data were evaluated using Rietveld analysis based on the structure data reported by Bolton *et al.* [16].

¹H NMR analysis was carried out at 300 K and 400 MHz using a Bruker spectrometer. 16 scans were averaged. 0.1 g sample was dissolved in 1 g deuterated dimethyl sulfoxide. Fourier transformation and phase correction were carried out using SpinWorks 4.2.10.0 ©2019, Kirk Marat. Peak integration was carried out using OriginPro version 2019 9.6.0.172, OriginLab Corporation, Northampton, MA, USA.

HPLC analysis was carried out using an Agilent 1100 HPLC system equipped with a binary pump and a diode array detector. The injected sample of 1 µL was separated on a Kintex 2.6 µm C18 100Å 100×4.6 mm column with pre-column. A mixture of ACN and water was used as the eluent. The eluent composition was gradually changed over time. Time 1 min: 10% ACN, time 20 min: 50% ACN, time 22 min: 95% ACN, time 27 min: 95% ACN, time 28 min: 10% ACN, post-time: 11 min. The eluent flow was 0.6 mL min⁻¹. The column was heated to 308 K during the analysis. Data analysis was carried out using Agilent ChemStation. The quantification of the impurities was carried out under the assumption that the impurities exhibit the same responsiveness at the measurement wavelength of 255 nm.

Field emission- scanning electron microscope images were taken by a Zeiss SUPRA 55 VP. The samples were prepared by sputter-coating with Au/Pd (80/20). 1.5 kV was chosen to prevent sample decomposition, but still, some images of higher magnification show the formation of bubbles under the metal coating as the result of the irradiation. The height-to-width ratio was determined from these images by measuring the height of crystals and dividing this value by the length of the crystal facet visible. Between 20 and 45 crystals were analysed for each batch.

Impact and friction determination were carried out according to DIN EN 13631-3 and DIN EN 13631-4.

Photomicrographs were taken using a Leica DMC4500 camera equipped with a Leica Z16APO objective. A SCHOTT KL 1500 electronic light source equipped with an Omnilux 15 V/150WZ-6.35 halogen light bulb was attached to the microscope stand. The images were processed via Leica LAS X software. The image pixel size was 0.702 µm for all taken photomicrographs. This resolution is a compromise between detectable defect size and field of view. It is assumed that defects of the size of 2–5 µm can be resolved via brightfield photomicrographs. Even smaller defects should be visible in dark-field photomicrographs (Figure S19)

which could be utilised to compare crystal batches of extremely high quality. Between 180 and 254 individual images were taken for each batch to ensure statistical significance of the results. The crystals were immersed in a mixture of 1:0.125 mL 1-methyl naphthalene and decane. This mixture was chosen as a compromise between highlighting the internal defects and the crystal edges. If the refractive index matches too well, the edges become undetectable. If, however, the refractive index is mismatched too strongly, the internal defects might be overshadowed by surface refraction of the crystals. The algorithm used for the automated crystal quality analysis was developed by Lins, Heisel, and Wohlgemuth and is available for download [12]. A composite image produced by the algorithm is displayed in Figure 1. The degree of crystal defects (DoCD) and the position of crystal defects (PoCD) [12] is used to judge the crystal quality. These values are obtained individually for every detected crystal. After binarization of the image, the dark area caused by the crystal edge is detected and excluded from analysis. The remaining area of the dark pixels within the crystal boundary is detected, and the DoCD is calculated by dividing the dark area by the crystal area. The PoCD is determined by the position of the dark pixels relative to the centre of the detected crystal. The crystal size is calculated as the equivalent diameter, i.e. the diameter of a circle of equal area. Because these values are calculated based on a binarized two-dimensional image of the crystal, the values have only limited absolute expressiveness, but are an excellent tool for crystal quality comparison, as long as the photomicrographs have been taken under strictly the same circumstances. The dark area resulting from the crystal edges is automatically detected and removed, and typically all dark pixels in the analysed area are caused by internal defects. Three major disturbances (Figure 1), however, occur that influence the determined DoCD (and consequently the PoCD) of a crystal. The distribution and the average of the determined DoCD and PoCD are heavily in-

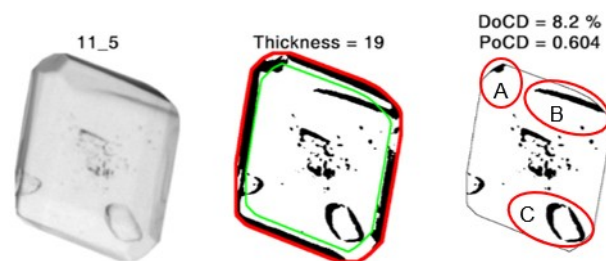


Figure 1. Visualisation of the automated detection process. Left: detected crystal. Centre: binarized image. The edge area that is excluded from detection is highlighted (area between red and green boundary). Right: analysed area of the detected crystal. Visualisation of the three main disturbances of the DoCD and PoCD determination: A) dark spots caused by the flattened edge of the crystals B) dark spots caused by surface defects C) dark spots caused by small crystals lying on the detected crystal.

fluenced by these disturbances. Manual removal of detected crystals was, therefore, required. The number of crystals that need to be removed can be drastically reduced if a very strict exclusion of smaller crystals is achieved during classification of the crystals. To be able to estimate the human factor in the process of selecting undisturbed detected crystals and to gain a feeling for the expected deviation of the obtained distributions and averages, two strategies were pursued. In one filter process, all detected crystals were removed that showed even the most miniscule trace of one of the abovementioned disturbances. In another filter process, only severe cases were removed. The resulting average DoCD values are visualised in Figure 2. The average crystal quality improves as expected for all batches by removing the affected crystals. And while the differences between the DoCD values of the untreated and the mildly treated data vary strongly between batches, the difference in DoCD between mildly and severely treated data is far more uniform between batches. This indicates that the re-

moval of strong disturbances improves the quality of the data and that the human factor involved in the removal of the disturbances seems to be weak. In this paper, the obtained DoCD and PoCD distribution of the strictly treated data is utilised for comparisons, because surface defects are here excluded and these defects do not influence crystal purity and density, and their inclusion would, therefore, reduce the correlation to the other analysis methods. But the strict exclusion may overestimate the crystal quality to some degree because crystals that exhibit internal defects that look like surface defects are excluded. Therefore, halving the difference between the DoCD values of mild and severe treatment is assumed as an error interval.

The SBRC batches were sieved to produce a size fraction close to 150–250 μm . These sieve fractions were used for all analysis. This was done for two reasons. On the one hand, fine particles disturb the analysis of coarser particles in the image processing as shown above, and on the other hand, for assessment of a crystallisation technique, the crystals close to the desired size are of most importance, because these are the crystals grown from the added seed crystals and not the product of secondary nucleation. Only they, therefore, can be used to judge the impact of the seed crystal quality and the seeding procedure on the product crystal quality. Because only 1 g of A1 is available, no sieving could be performed without significant material loss in the process. Here, after image processing, based on the crystal size, a certain amount of data sets was removed to obtain a normal distribution centred around 200 μm . This data ensemble is called A1norm. To retain correlation between the image processing data and the data of the other analysis methods for A1, analysis of the image processing was carried out for the non-normalised data in addition to the normalised data.

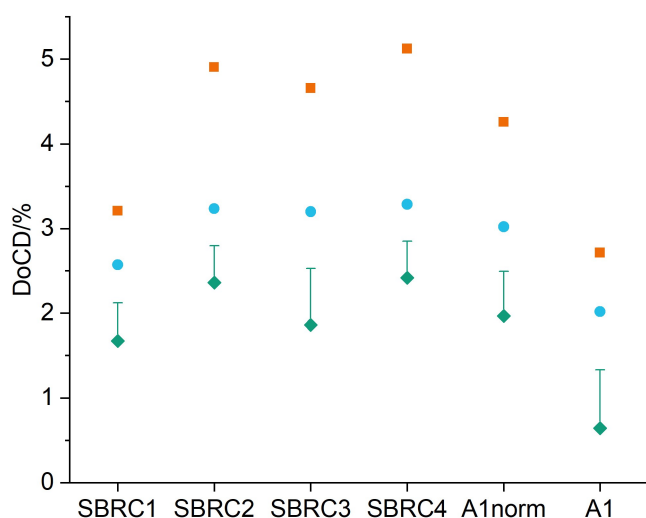


Figure 2. Determined average DoCD values of the crystal batches. Orange squares: no data treatment, teal circles mild data treatment, green diamonds strict data exclusion. Error bars represent half the difference between mild and severe data exclusion.

3 Results

3.1 Conventional Approaches

Analysis results are summarised in Table 1. Representative photomicrographs are displayed in Figure 3. All cocrystal

Table 1. Analysis data of the cocrystal batches.

	BRC1	SBRC1	SBRC2	SBRC3	SBRC4	A1
purity (^1H NMR)/%	98.95	99.39	99.48	99.31	99.54	99.68
purity (HPLC)/%	99.87	99.62	99.89	99.62	99.93	99.84
phase purity/%	100	100	100	99.91	100	99.93
solvent content/mass%	0.19	0.01	0.01	0.02	0.01	0.01
skeletal density/ g cm^{-3}	1.9533	1.9545	1.9544	1.9540	1.9553	1.9545
impact sensitivity/Nm	4.5	1.5	2	2	1.5	3
friction sensitivity/N	192	120	144	144	160	120
decomposition onset/K	492.05	491.85	490.25	490.95	491.15	491.15
$D(4,3)/\mu\text{m}$	35	163	137	159	179	160
height-to-width ratio	n.d.	0.60	0.80	0.62	0.71	0.55



Figure 3. Representative photomicrographs of BRC1 (top left), A1 (top right), SBRC1 (mid left), SBRC2 (mid right), SBRC3 (bottom left), and SBRC4 (bottom right).

batches are more than 99.9% phase pure and exhibit a chemical purity between 99.62% (SBRC1 and 3) and 99.93% (SBRC4) based on HPLC. Based on ^1H NMR, the purity ranges between 98.95% (BRC1) and 99.68% (A1). BRC1's solvent content is almost 20 times higher than the solvent content of SBRC1,2,4 and A1. SBRC3 possesses a slightly higher solvent content than the other SBRC batches. The skeletal density of BRC1 is, based on the determined precision of helium pycnometry [15], barely significantly less dense than the other batches, whereas SBRC4 is barely significantly denser than the other batches. All densities lie within a 0.002 g cm^{-3} interval and are on average 0.009 g cm^{-3} higher than the density reported by Bolton *et al.* [16] BRC1 possesses the best impact and friction sensitivity of the tested batches. The decomposition onset in DSC analysis of all batches lies within an in-

terval of 1.8 K. SEM images (Figure S1–S6) show that all crystals exhibit a mostly smooth crystal surface.

3.2 Digital Image Processing

The crystals obtained from BRC experiments are too small, irregular, and intergrown to be analysed via image processing.

The DoCD and the PoCD of the SBRC and A1 crystals have been analysed and the results are visualised in Figure 2, 4, 5, and Table 2.

The SBRC DoCD distributions can be satisfactorily described by a Weibull distribution [17]. No satisfactory fit, however, was achieved for A1 and A1norm. From Figure 4 it can be seen that A1's and A1norm's distribution maximum is the first bin between 0 and 0.25% DoCD, whereas the maxima for the SBRC batches are reached between 0.25 and 1.5% DoCD. SBRC1 possesses the narrowest distribution except for A1. Considering the proposed error margin, the average DoCD of A1 is significantly smaller than the average DoCD of all other batches. The average DoCD of SBRC1 is significantly smaller than the average DoCD of SBRC2 and 4, and the average of A1norm is indistinguishable from the averages of SBRC1,2,3, and 4. The DoCD of A1 and A1norm is strongly crystal size dependent (Figure S17). This can easily be seen from the difference in average DoCD between A1norm and A1 in Figure 2. A1 shows a strong increase in DoCD with increasing particle size. For SBRC1 and 3 a weak increase in DoCD with particle size is observed, but for SBRC2 and 4, a weak decrease in DoCD with increasing particle size is present (Figure S13–S16).

The distribution of PoCD of all batches can be approximated by a normal distribution (Figure S7–S12). Their distribution is visualised as the respective box plot (Figure 5) [18]. The distribution of the PoCD is wider for SBRC2 and A1norm than of the rest. The medians of all batches lie close to 0.5 PoCD. Only A1 exhibits PoCD smaller than 0.15 while all batches possess PoCD greater than 0.85.

Table 2. Image processing data of the cocrystal batches.

	SBRC1	SBRC2	SBRC3	SBRC4	A1norm	A1
nr. of detected crystals	1474	1282	1257	1182	3071	3071
nr. of evaluated crystals	610	267	445	301	286	1963
average DoCD/%	1.7	2.4	1.9	2.4	2.0	0.6
error margin of average DoCD/%	0.4	0.4	0.7	0.4	0.5	0.7
median of DoCD/%	1.2	1.5	1.2	1.7	0.8	0.0
average PoCD	0.46	0.52	0.45	0.43	0.47	0.49
median PoCD	0.43	0.51	0.44	0.41	0.46	0.46

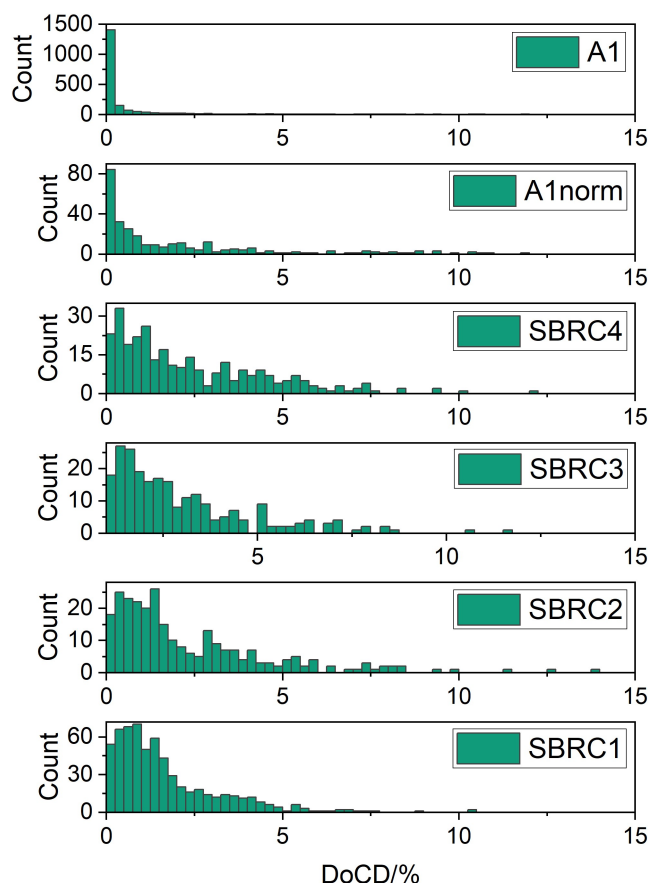


Figure 4. Distributions of DoCD for all batches. All bins are of size 0.25 %.

4 Discussion

The purity data obtained from HPLC and ^1H NMR are in good agreement (except for BRC1). The average offset between the data of 0.3 % is most likely the result of different sensitivities of the two methods towards the compounds. The lower ^1H NMR purity of BRC1 is the result of its higher ACN content caused by the more rapid crystallisation. The solvent inclusion does not lower the HPLC purity, because ACN is not detected via the HPLC method. Cocrystallisation improves chemical purity compared to the raw material, but the prolonged exposure to elevated temperature during the crystallisation increases signal intensity of some impurity signals, and even new signals occur, in the SBRC experiments (Tables S1 and S2). The significantly lower purity of SBRC1 and 3 compared to SBRC2 and 4 is caused by the utilised nickel plated magnetic stir bar, which led to a weak brown discolouration of the crystallin product. For SBRC2 and SBRC4 the stir bar was coated with epoxy resin to prevent any chemical reaction. The varying amounts of impurities seem to not influence the decomposition temperature in DSC measurements. Because of the faster crystallisation of BRC1, RDX impurity can only be found in

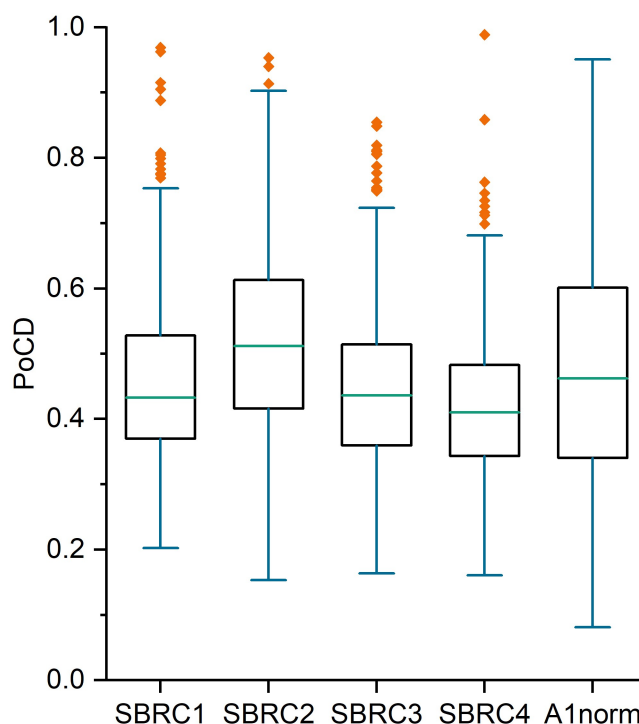


Figure 5. Box plots of the PoCD values of the evaluated batches. The green horizontal line represents the median of the data, the box represents the position of 50 % of the data, the blue so-called whiskers indicate the data that lie within 1.5 times the box height (interquartile range IQR), and the orange rhombs visualise the outliers.

this cocrystal batch in the ^1H NMR and HPLC. The lower impact sensitivity of BRC1 compared to the SBRC batches might be considered significant, but is most likely the result of the smaller particle size or the more clustered particles. In the past, four BRC batches produced in a similar fashion and of similar particle size possessed an impact sensitivity between 1 and 2 Nm. The impact sensitivity of 4 Nm might, therefore, be anomalous.

Based on studies carried out for RDX where the determined density was linked to the amount of internal defects [7,8], a strong correlation should be expected between the DoCD values of the cocrystal batches and the determined densities. No such correlation, however, exists between the determined data. The significantly better average and median DoCD values of A1 compared to SBRC1 and the significantly better values of SBRC1 compared to the other SBRC batches disagree with the determined density values. A1 should exhibit the highest density followed by SBRC1. The precision of pycnometric density determination of explosives has been previously studied [15] and based on these results it can be stated with statistical backing that the density of SBRC1 is not significantly different from the density of SBRC2 and SBRC3 and that SBRC4 is slightly, but significantly denser than the other SBRC batch-

es. The measurement error of A1's density determination is larger (0.0012 g cm^{-3} compared to 0.0003 g cm^{-3}) because it was determined in a smaller sample cell. Still, within these limits, A1 cannot possess a significantly higher density than SBRC4. Considering that the average DoCD of SBRC4 is significantly higher than the average DoCD of SBRC1 (and of A1), this is exactly an inverse correlation between DoCD and skeletal density. Because of a lack of a significant crystal size dependency (Figures S13-S16) of the SBRC experiments, the increase in crystal height seems to be of lesser importance to the DoCD values of these batches. This, consequently, means the DoCD value need not be adjusted for the difference in height-to-width ratio between the batches. The varying height-to-width ratios between batches (Table 1), hence, should not be responsible for the discrepancy between density and DoCD. The relatively high density of BRC1, despite its high solvent content, indicates that A1 and the SBRC batches possess significantly more gas inclusions. This might be the result of the ongoing decomposition of CL-20 during the crystallisation, and BRC1 exhibits, because of the fast crystallisation, considerably less decomposition than SBRC1,2,3 and A1. The higher density of SBRC4 could also correlate with the lower decomposition content compared to the other SBRC batches and A1. This agrees with SBRC4 having the shortest crystallisation time of all SBRC batches. The image processing does not differentiate between gas and liquid inclusions, but in conjunction with density measurement and solvent content determination, differentiation seems to be possible.

The PoCD values can give insight into the cause of the crystal defect. Preliminary antisolvent crystallisation batches showed a strong variation of the PoCD. Eccentric defects were the result of crystal edge damage caused by abrasion, while defects located in the centre of the crystals indicated insufficient seed crystal dissolution (Figure S20). The intermediate values for all tested batches in this paper and their substantial standard deviation, however, do not allow for a conclusion based on PoCD.

Based on the various crystal analysis methods, the following statements can be made.

The purification of the raw material by cocrystallisation is to some degree offset by the increased decomposition products present in the cocrystals of A1 and SBRC batches. A reduction of crystallisation time might improve the crystal quality. All SBRC batches are indistinguishable from A1norm via image processing, and no significant difference between the SBRC batches and A1 exists in the other analysis methods (except for the slightly higher density of SBRC4). The average DoCD values of the SBRC batches and A1norm lie around 2% which corresponds to a quite pristine-looking crystal as can be seen from the comparison in Figure S18. SBRC is, thus, capable of producing coarse CL-20/HMX cocrystal in the pilot plant scale with the same crystal quality as antisolvent crystallisation in the laboratory scale. A1, however, exhibits a significantly better average DoCD than the SBRC batches, because of the sizeable amount of small-

er crystals with a DoCD of 0%. This means that by applying image processing of photomicrographs a significant differentiation between A1 and the SBRC batches was possible while no established analysis method, with the possible exception of neutron scattering [19] and density flotation, [20] could yield significant results. Great advantages of image processing are that no exotic equipment is needed for the analysis and that extremely small sample quantities are required. This makes this method ideal for the further development of crystallisation experiments, especially in the laboratory scale. More thorough removal of fine crystals before analysis is required to reduce the DoCD error bar sizes. Even though no image processing of BRC1 was possible and the density is only marginally lower than the densities of the other batches, it is obvious from the photomicrograph (Figure 3) and the SEM image (Figure S6) that the crystal quality is not as good as the crystal quality of the other batches.

5 Conclusion

^1H NMR and HPLC showed that the chemical purity of the obtained cocrystals from antisolvent crystallisation and SBRC is higher than the chemical purity of the raw material. Image processing was used to determine that the DoCD of SBRC is not crystal size dependent but the DoCD of laboratory-scale antisolvent crystallisation is. Furthermore, it was found that SBRC is capable of producing the CL-20/HMX cocrystal in a pilot plant scale in a size range of 150–250 μm with the same crystal quality as laboratory-scale antisolvent crystallisation. Because of the small required sample mass, digital image processing is a valuable tool for crystallisation optimisation especially in the laboratory scale and is capable of comparing samples of vastly different production scales. Further work is required to correlate the determined DoCD values with shock sensitivity tests and to reduce the error bars of the average DoCD values.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SHORT COMMUNICATION



D. Herrmannsdörfer, T. M. Klapötke*

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**Quality Assessment of the CL-20/
HMX Cocrystal Utilising Digital
Image Processing**

