# INVESTIGATION OF THE MICROSTRUCTURE OF ADN-PRILLS USING 2D-X-RAY DIFFRACTION

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## Abstract

Ammonium dinitramide (ADN) is the upcoming oxidizer for solid propellants. Spherical ADN particles, so-called ADN-prills, are a key product for the development of environmental friendly and low-signature solid propellants for defense and space applications. The particle size and the spherical shape of the ADN-prills can be controlled by the emulsion crystallization process or by spray congealing processes. In this work the microstructure of ADN-Prills was investigated by 2D-X-ray diffraction. This leads to a more profound knowledge about the crystal structure of ADN-prills and gives the opportunity to produce enhanced ADN particles for propellant applications.

## Introduction

Ammonium dinitramide (ADN, $NH_4N(NO_2)_2$) is a promising halogen-free oxidizing agent for solid rocket propellants for defense and space applications. To obtain propellant formulations with high specific impulse the particles should have a spherical shape. Raw ADN from synthesis has a needle or plate like shape, which is caused by its crystallization kinetics. Due to this material property it was not possible to produce applicable ADN particles by crystallization from solvents so far. Spherical ADN particles, so-called ADN-Prills, must be produced. The mechanical behavior and stability of prills varies, and prills show different appearance and internal structuring. The material melts about 93.5°C and decomposition may start with the melting [1]. Besides, an early decomposition e.g. in applications with copper based catalysts [2] and the formation of eutectic mixtures with ammonium nitrate and with water are reported [3, 4, 5]. The properties and the crystal- and microstructure were investigated intensively in the last decades e.g. [6, 7], and structure modification are applied such as prilling and coating in order to improve stability, process ability or mitigate incompatibilities [8, 9]. However,

there is little known about the interaction and stabilization mechanisms on the micro and crystal structure level. Therefore, systematic investigations by means of temperature resolved X-ray diffraction were started [10, 11]. The product design, properties and micro structure of ADN-prills are reported elsewhere [12, 13].

## Crystal structure of ADN

The crystal and molecular structures of ammonium dinitramide (ADN) were investigated with X-ray diffraction by Gidaspov et al. in 1995 [14]. ADN forms crystals of the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The lattice parameters are a = 6.84, b = 11.90, c = 5.61 Å, respectively, with the angle $\beta = 99.8°$ and the density $\rho = 1.84(2)$ g/cm$^3$. The crystal structure is shown in Fig. 1 and the molecular structure of the anion $N(NO_2)_2^-$ in Fig. 2.

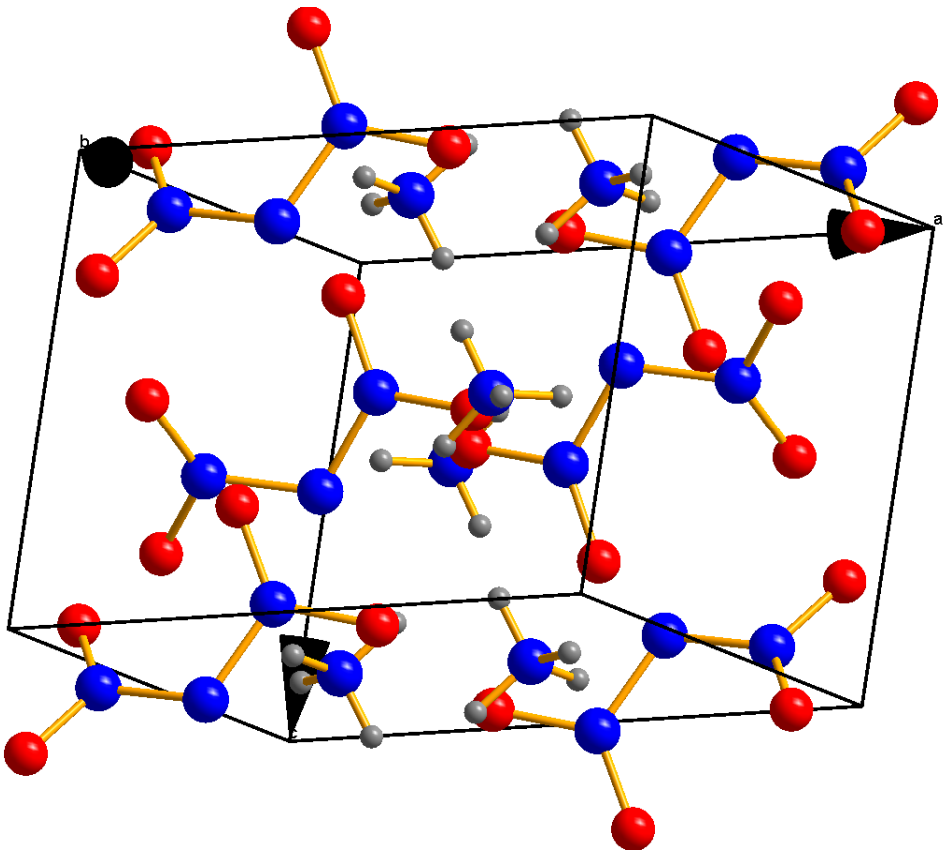


Fig. 1: Crystal structure of ADN [15].

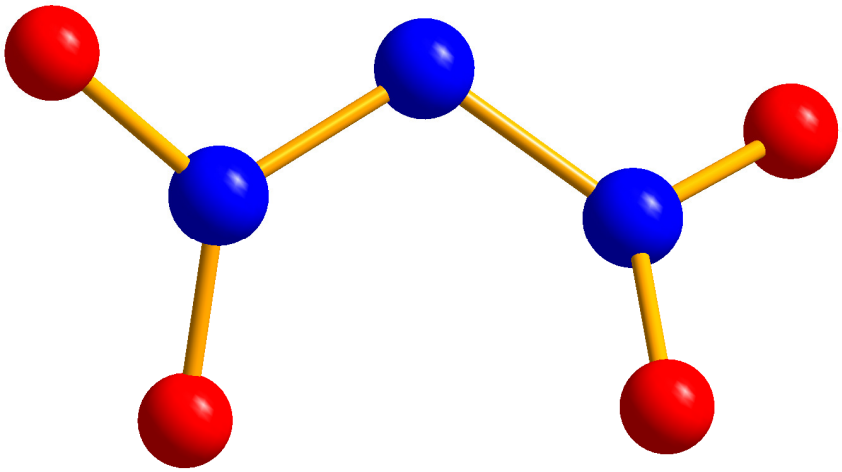

Fig. 2: The molecular structure of the dinitramide anion.

## Manufacturing of the ADN-Prills

ADN-Prills may be produced by the dispersion of ADN melt and subsequent recrystallization of the molten droplets into solid, spherical particles. This is possible by spay processes or by an emulsion crystallization process developed by Fraunhofer-ICT. ADN-prills of different particle sizes [16] were produced by the emulsion crystallization process (European patent EP 0 953 555 B1) which has four steps: In the first step of this process raw ADN is suspended in an anti-solvent, e.g. Paraffin. Then this suspension is heated up above the melting temperature of ADN. Under permanent stirring an emulsion of the desired droplet size is created. By cooling down the melt droplets are recrystallized, yielding the desired particle shape. The last step is the solid/liquid separation, washing and drying the product. The steps of the emulsion crystallizations process are shown in Fig. 3. In one case the resulting 500 g batch of ADN-prills was separated in tree fractions by sieving for subsequent investigation. Regarding the microscope pictures (by Leica Z16 APO) of the sieve fractions (Fig. 4 - 6) it became obvious that the mid-size and large fraction contain more prills with layer structures and fragmented spheres, some of them disc-shaped. The small prills were in good order and show only few layer-structured particles.

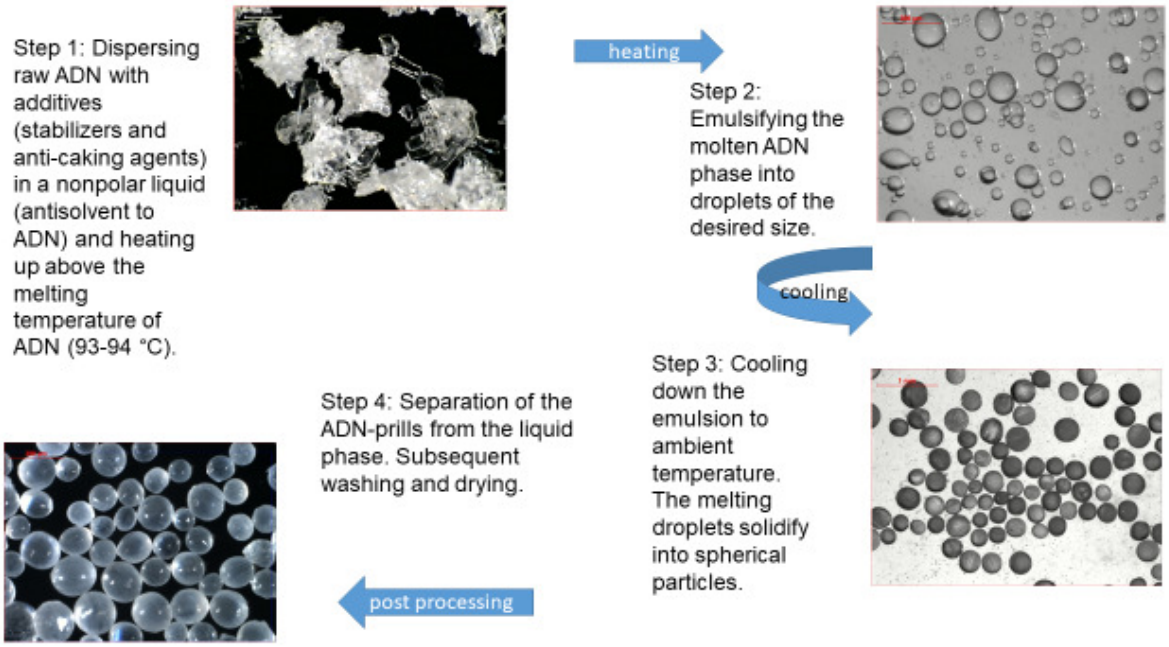


Fig. 3: Emulsion crystallization process by Fraunhofer-ICT.

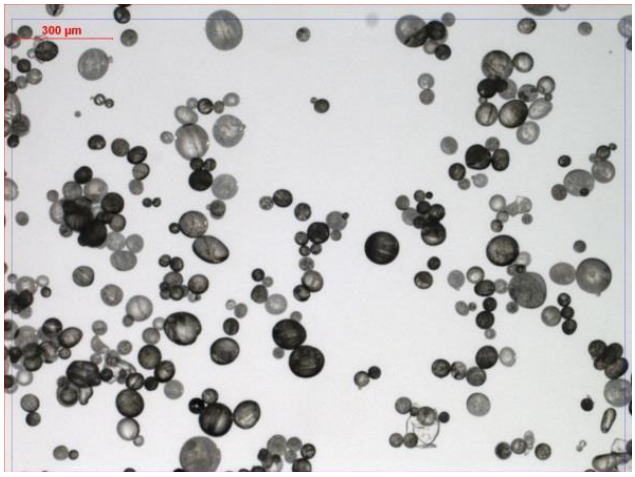


Fig. 4: ADN-prills, sieve fraction < 125 µm.

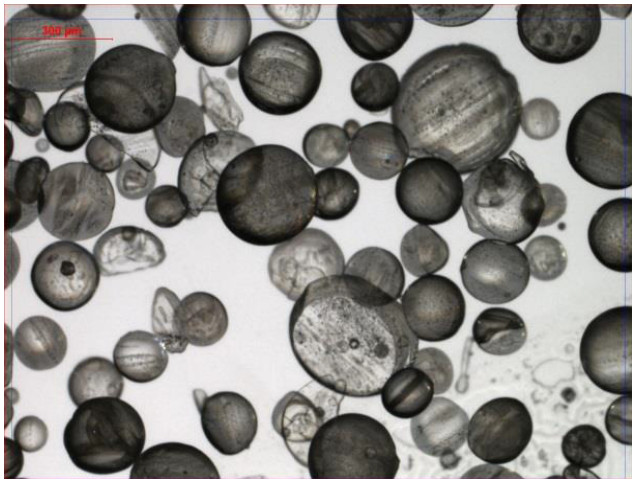

Fig. 5: ADN-prills, sieve fraction 125 – 355 µm.

Fig. 6: ADN-prills, sieve fraction > 355 µm.

## Measurements with area detector (2DXRD)

Selected individual prills of the sieve fractions were investigated on a diffractometer D8 Discover equipped with copper tube, micro focus mono capillary, Eulerian cradle with xyz-stage, laser/video positioning system, and micro gap area detector VANTEC-500 from Bruker AXS (Fig. 7). The system provides a minimum spot size of the X-ray beam of 50 µm. The exposure time per position was 300 s.

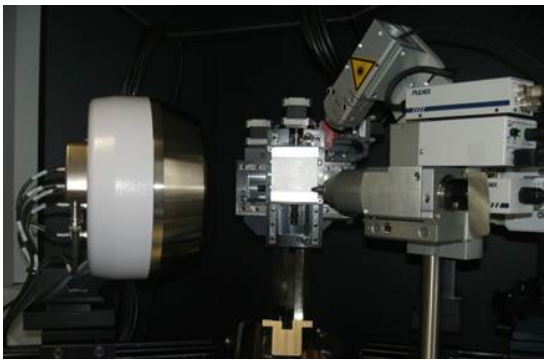

Fig. 7: X-ray diffraction system equipped with Eulerian cradle, xyz-stage (back), micro gap area detector (left) and laser/video positioning system (front right).

## Results and discussion

A region between 29.18 and 30.06 °2θ was chosen for evaluation with ring cursor, beause temperature resolved investigations by means of X-ray diffraction showed strong peak fluctuation of the (040) peak of ADN about 29.8 °2θ (Fig. 8), which indicates changing preferred orientations of the crystal domains[11]. The 2D-picture of prills of the sieve fraction <125 µm is shown in Fig. 9, of 125 – 355 µm in Fig. 10 and of >355 µm in Fig. 11, respectivly.

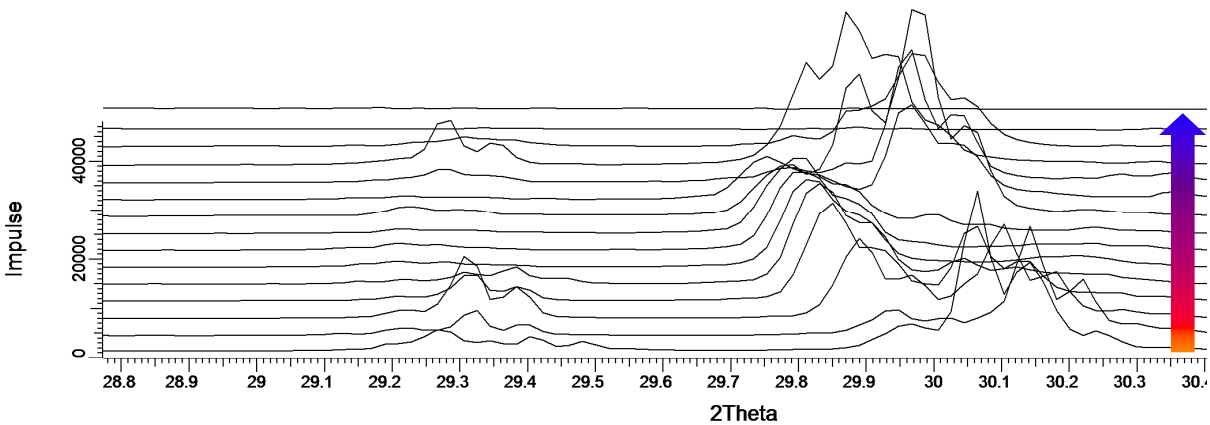


Fig. 8: Section of diffraction patterns of raw ADN with intermediate leftward shift/switch of the (040) peak during heating from 30 to 93 °C (bottom to top) [11].

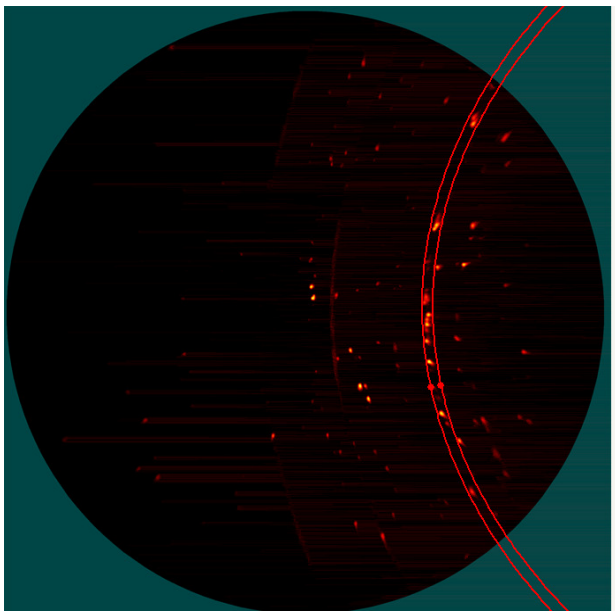

Fig. 9: 2D-picture of the sieve fraction <125 µm with ring curser in the region 29.18 – 30.06 °2θ.

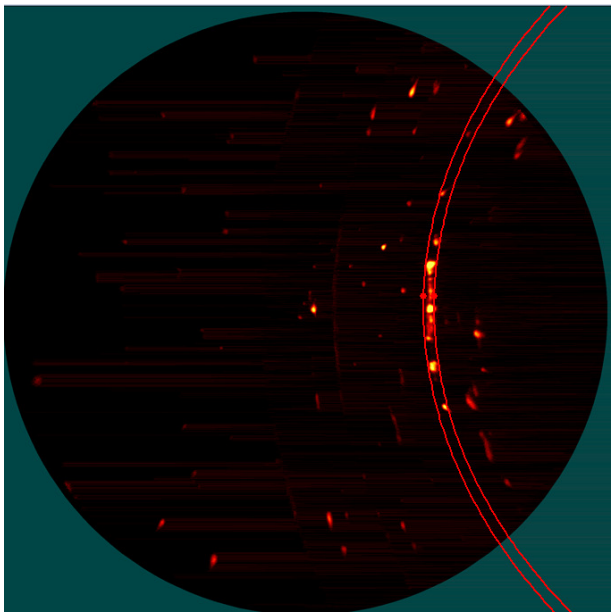
Fig 10: 2D-picture of the sieve fraction 125 – 355 µm with ring curser in the region 29.18 – 30.06 °2θ.

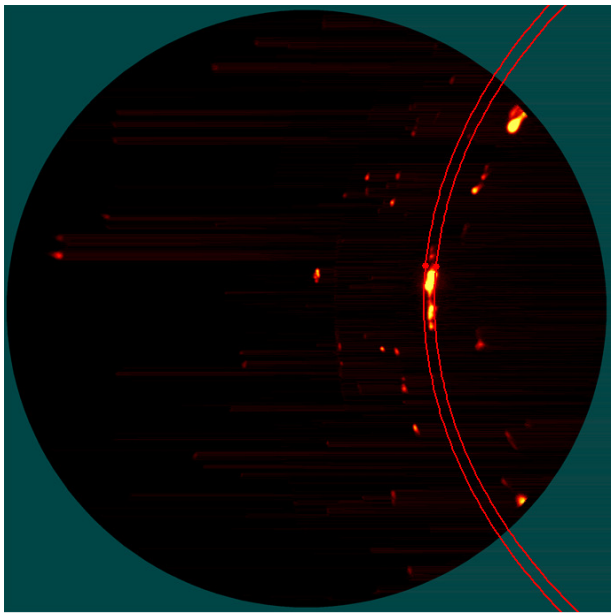
Fig. 11: 2D-picture of the sieve fraction >355 µm with ring curser in the region 29.18 – 30.06 °2θ.

The evaluation of the 2D-images with ring cursor and gamma integration yielded the intensity distribution along the ring cursors, the gamma scans, shown in Fig. 12.

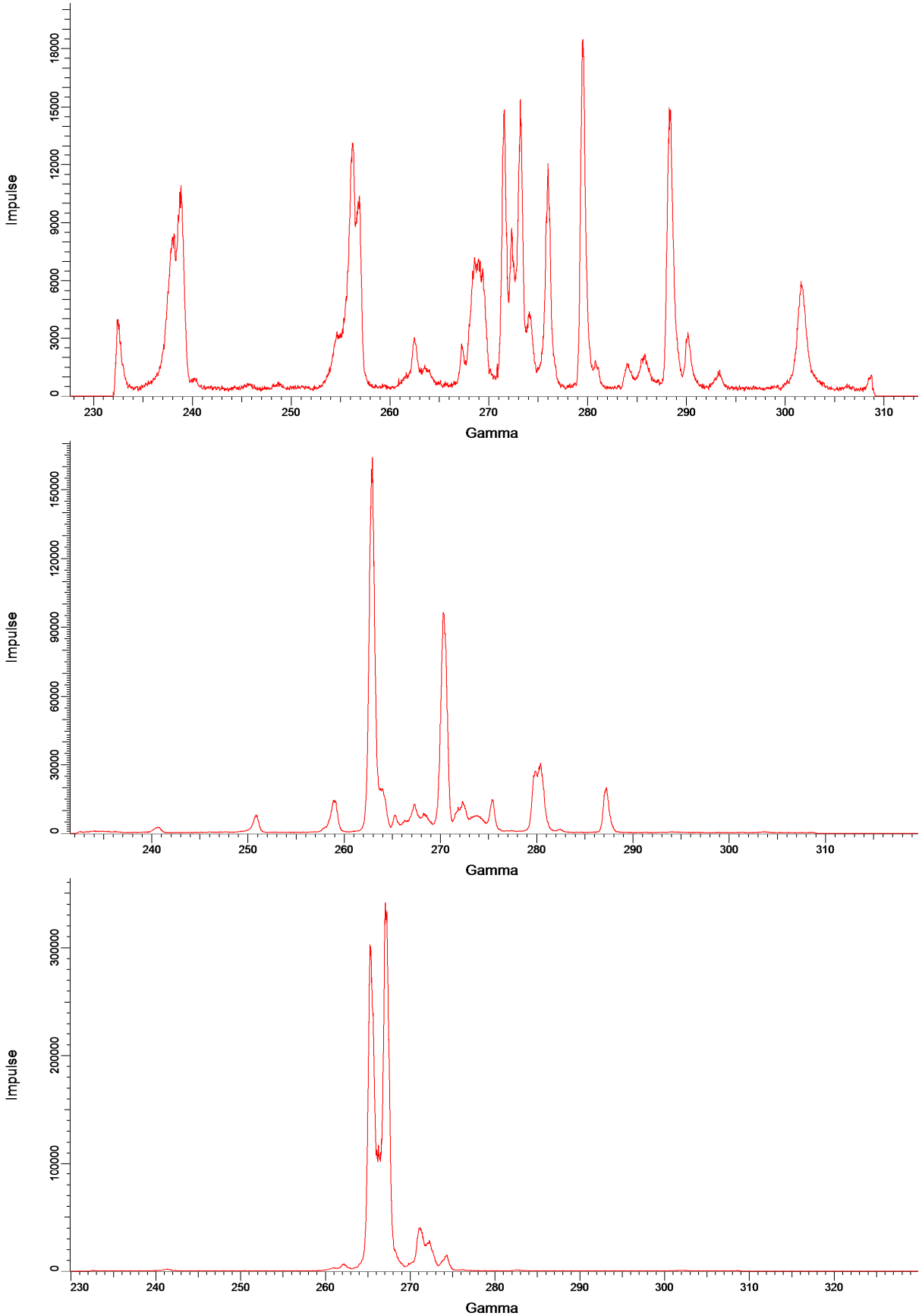


Fig. 12: Comparison of the integrated gamma scans of the evaluation presented in Fig. 9 (<125 µm, top), Fig. 10 (125 – 355 µm, middle) and Fig. 11 (>355 µm, bottom).

The evaluation confirms that an investigation of individual prills with micro focus and 2D detector is possible. The 2D-pictures and the gamma scans of the sieve fractions show a broader distribution of reflections for the small ADN-prills (<125 µm), whereas the larger prills (125 – 355 µm and >355 µm) show less but more accumulated spots. The effect might be explained by large anisotropic crystal domains with significant preferred orientation in large prills compared to a homogeneous crystal orientation of smaller domains in the small prills.

## Outlook

Further investigations with broader variety of prill qualities are necessary to confirm these observations, and a correlation with mechanical behavior should be made. Besides, crystallite size/strain analysis via XRD rocking curve approach could help to develop concepts for prill quality assessment of ADN via XRD in future.

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