XRD and TGA as methods for evaluation of structural damage of textiles on a macro scale during a household tumble drying process

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Household textiles are exposed to washing and drying cycles over the use stage (textile care). Textiles are in contact with water, chemicals, high temperatures, and mechanical stress during both processes, affecting their appearance and usability. The laundry and drying process in a rotating drum causes thermal and mechanical stress (cyclic deformation, abrasion), which may cause damage down to the molecular scale. By using inadequate parameters, drying becomes one of the most aggressive processes during daily garment usage, resulting in changes in the physical and mechanical properties of fibres/textiles, affecting the shortening of the garment's lifespan.
Having this in mind, the research carried out within the project "Low emission household tumble drying with an evaluation of damage to textile materials" focuses primarily on the identification and evaluation of changes at the molecular scale, exerted by the exposure of the respective fabrics to an increased number of wetting/drying cycles. To this end, X-ray diffraction (XRD) and thermogravimetric analysis (TGA), were applied to examine the alteration in crystallinity and thermal degradation profiles, respectively. The research was conducted on a wide range of fabrics, i.e., cotton, polyester, cotton/polyester blend, wool, silk, polyamide, polyacrylonitrile and viscose.
***Keywords**: Drying, fibres, damage, XRD, TGA, crystallinity.*

1. Introduction

From the point of view of the sustainable use of textiles, it is impossible to overlook the aspect of textile care, especially the tumble-drying process of textiles in the domestic household. It is known that the tumble-drying process intensively involves various mechanical processes, such as continuous beating, falling, entanglement, and rubbing of the fabric itself, as well as aggressive agitator actions and repeated actions by high temperature and humidity airflow [1]. To achieve a better drying effect, it is necessary to understand the properties of used textile material and the effects of humidity, temperature, time and drying process parameters on drying efficiency and material degradation. Several studies were found in the literature that analysed the impact of different parameters on drying efficiency, and very few studies would evaluate the impact of the drying process on fibre chemical

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structure, crystallinity, and microstructure and systematically analyse fabric damage during drying. Higgins [2] investigated the effects of moisture content, temperature, and time of the first drying cycle on the dimensional stability and appearance of cotton knitwear and fabric. Otzurk [3] monitored the influence of repeated drying cycles, as well as the structure of viscose single jersey fabric, on the change of its dimensional and physical properties. Yu [4] conducted a study on the effect of temperature and drying time on the wrinkling properties of cotton fabric and reported that material wrinkling occurs in the last stage of drying. Wei [1] reported on optimising the drying process at large loads and the non-ironing procedure for a small load of silk fabrics. He monitored the change in the appearance, mechanical properties, and microstructure of silk fabric before and after drying with various drying parameters (heat power, air velocity and drum-rotating speed) and found that the drying efficiency of the silk fabric is more sensitive to air velocity (humidity of drying-air) rather than heater temperature. It is known that textiles have their moisture regain, i.e., bound or hygroscopic moisture. The highest amount of hygroscopic moisture at 20°C and 65% RH is absorbed by wool (14.5%), followed by cotton (7.4 - 9.5%), while synthetic fibres absorb between 0.0 and 4.4%, in contrast to regenerated viscose fibres with 11.5-13.5%. Yun reported that 3 kg of bone-dried cotton, which required 244 Wh of energy for drying, was absorbed in 20 °C and 65% RH, 222g of moisture [5]. Bengtsson highlighted the phenomenon of over-drying the textile material, which should be avoided due to the permanent deformation of textile fibres [6].

Fibres have different degrees of structural order, translating into specific fabric behaviour on a macro scale. Structural differences in fibres mainly originate from the production process; in natural fibres, the crystalline regions develop during the growth stage, while in the case of synthetics, the crystallinity forms during oriented stretching/stabilisation of fibres. The structural characteristics, mainly the degree of crystallinity or crystalline/amorphous ratio, guide final fabrics' mechanical and thermal resistance. Having this in mind, the methods like thermogravimetric analysis (TGA) and X-ray diffraction crystallography (XRD) can be of use for the prediction of changes at the fibres' molecular scale, which can be exerted by the exposure of fabrics to numerous wetting/drying cycles in the household textile care. TGA method is widely used for predicting materials` thermal stability, detecting the weight change of a substance as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. As such, it may detect processes, such as evaporation, decomposition, oxidation and other effects of temperature change that cause mass changes, indicating desorption/sorption ability of moisture or volatile agents, materials` degradation, oxidative processes, etc. The apparatus used for TGA analysis consists of a highly sensitive balance to measure weight changes and a programmable furnace to control the heat-up rate of the sample. The balance is located above the furnace and is thermally isolated from the heat. A high-precision hang-down wire is suspended from the balance down into the furnace. At the end of the hang-down wire is the sample pan, the position of which must be reproducible. The balance must be isolated from the thermal effects (e.g., by use of a thermostatic chamber) to maximise the sensitivity, accuracy, and precision of weighing.

On the other hand, the XRD method is used for investigations of solid crystalline samples (identification and quantitative analysis of different phases, degree of crystallinity, crystal lattice dimensions and crystal sizes), whereby the study is based on the coherent scattering of X-rays by electrons in atoms. The rays are diffracted in a pattern determined by the position, arrangement, and size of the constituents of the crystal. Scattered photons, which may undergo subsequent interference, lead to a characteristic diffraction pattern specific to the crystalline powder and may serve as its 'fingerprint'. XRD is based on wide-angle elastic scattering and is generally used for ordered material (long-range order crystalline material) like fibres. Fibres in their structure combine ordered - highly crystalline areas, disordered amorphous areas and semi-crystalline areas. The degree of crystallinity is formed in fibres by heating above the glass transition temperature (Tg) and is often accompanied by molecular orientation (drawing, stretching). This occurs during fibre formation (extrusion) in the case of synthetic fibres and during growth in the case of natural fibres. The presence and relative amount of individual structural forms depend on how the polymer was formed and processed. The arrangement of the crystalline areas in the fibres is manifested by a higher degree of crystallinity, determined by the XRD method, which indicates good mechanical properties. As a result, the XRD method gives a diffraction curve - an XRD spectrum that shows the intensity

of the scattered rays at different diffraction angles.
The goal of the presented study was to evaluate the capacity of TGA and XRD analytical methods for predicting changes in fibres` structure at a molecular level and recognise the impact of the household tumble drying process on the physical and mechanical properties of textile material.

2. Materials and Methods

2.1. Materials

Over the whole research process, standardised fabrics were used, chosen according to the SIST EN ISO 60456, SIST EN 61121. Standardised fabrics, their surface mass and abbreviation are presented in Table 1.

2.2. Preparation of materials

The process simulating different wetting/drying procedures was designed as 25 cycles (imitating the household textile care) of repeated sample wetting and drying procedures. Samples were wetted using water corresponding to EN 60456: 2016 (ST=2.5±0.2 mmol/L; pH 7.5±0.2; T = 15±2°C). The wetting process was conducted on padder HVF 0978 Werner Mathis AG (CHE), operating with pressure of 1.5 bar and the roller rotating speed of 3 m/min. After the wetting, standardised fabrics were exposed to different drying procedures:

I. Photothermal drying (PT)
Photothermal drying was performed using moisture analyser DBS 60-3 Kern (DE) with halogen lamp of 400W. The time scale of drying step for each sample fabric is presented in Tab.1.

II. Microwave drying (MW)
Microwave drying was performed with an MO-17 ME microwave from Gorenje (SLO). The samples were microwave dried at 350W and a frequency of 2.450 MHz. The time scale of drying step for each sample fabric is presented in Tab.1.

III. Hot air drying (HA)
Samples were treated with hot air in the laboratory scale DHE 43687 Mathis dryer at constant temperature 80°C. The time scale of drying step for each sample fabric is presented in Tab.1.
The time scale of each drying process was determined according to the hydroscopic properties (ability of a textile fibre to absorb humidity from the environment) of individual fabric fibre composition. The drying time was evaluated as a time to achieve a maximum percentage of water that the fibre can absorb without appearing wet (hygroscopic water – moisture). The values of moisture content for individual samples and the drying time needed to achieve moisture content are presented in Tab.2. Drying times are presented for temperatures 60 and 80 °C.

2.3. Analytical methods

TGA analysis was performed to determine the changes in thermal stability resulting from changes in samples' molecular structure after different wetting/drying procedures. For the analysis, the Perkin Elmer TGA 8000 system was used (Fig.1 top-left). Small pieces of fabrics with mass [mg] were positioned onto standard ceramic pans. Before measurements, samples were conditioned at room temperature, without a pre-heating cycle, to obtain the water evaporation data. During the experiment, samples positioned within the ceramic sample pan were heated within the 25–400 °C temperature range, applying a heating rate of 10 °C/min under steady nitrogen.
XRD analysis was performed to evaluate crystalline/amorphous ratio changes upon different wetting/drying exposures using a desktop X-ray powder diffractometer BRUKER D2 Phaser - XRD. The crystallographic spectra were measured from 5° to 70°2Theta, by the increment of 0.03 at voltage 30 kV and current 10 mA, using Cu tube with 1.54184 Å.
Samples for the XRD method were prepared in the tablet form, where fabrics were firstly dissected in to individual yarn and cut in to small pieces. The cut samples were weighted, and the same mass (0.1 g) was used for the preparation of all tablets.

Table 1: Table of used standardised fabrics with their corresponding surface mass and time scale for drying step of individual sample fabrics in the repeated wetting/drying process

Sample	Abbreviation	Surface mass (g/m^2)	Moisture content (% at 65% RH)	Drying Time (sec)		
				PT	MW	HA
Cotton	CO	170	5,0	500	178	115
Polyester / Cotton (65/35)	PES/CO	170	2,0	365	126	77
Polyester	PES	170	0,5	330	150	115
Polyamide	PA	75	6,0	65	120	58
Acrylic	PAN	140	1,5	565	178	118
Wool	WO	125	14,5	260	150	53
Silk	SE	90	9,5	280	118	56
Viscose	CV	160	12	500	150	58

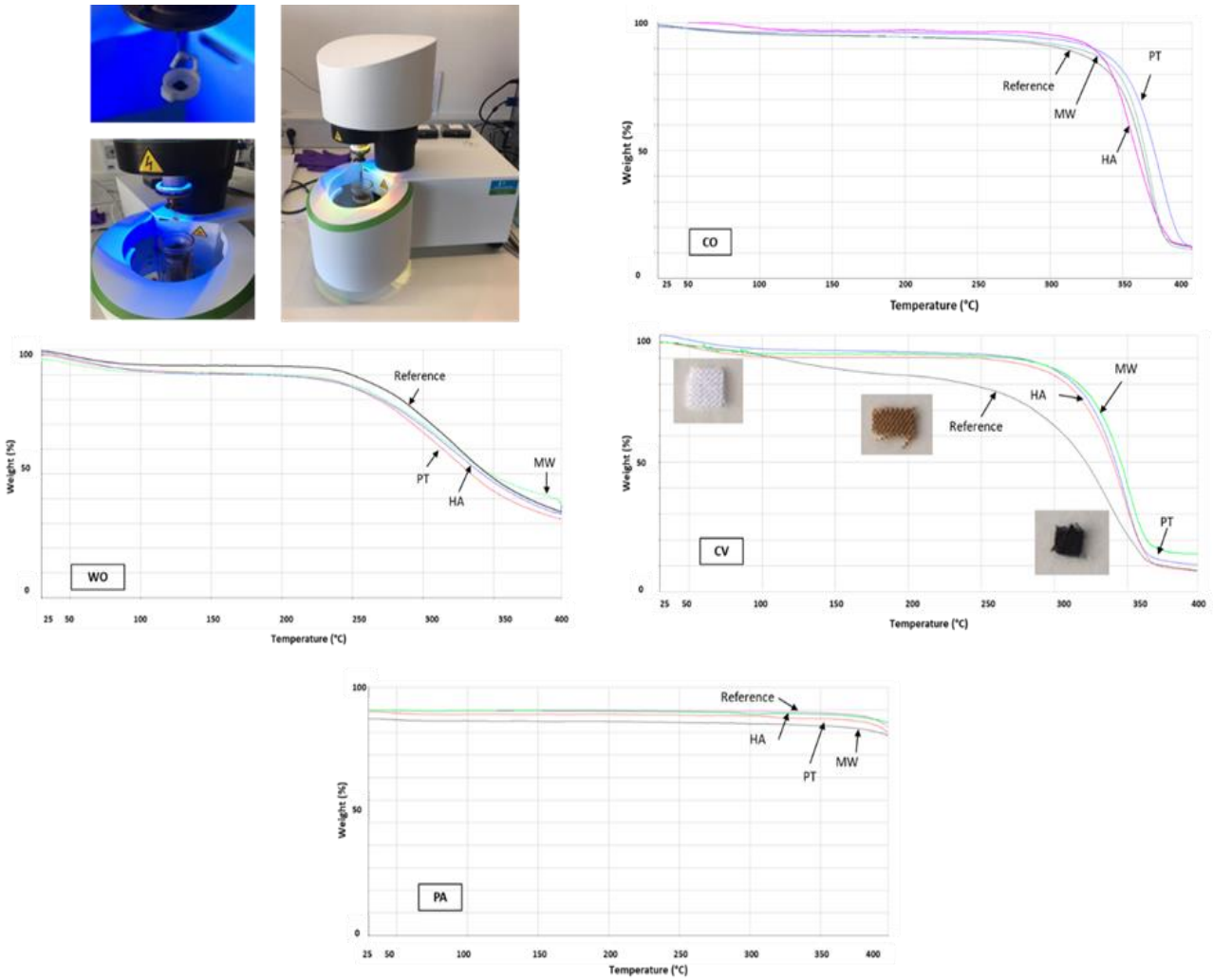

Fig.1 TGA apparatus (top-left) and composite thermograms for CO (top-right), WO (middle-left) and CV (middle-right) fabrics and PA (bottom) before and after 25 cycles of wetting/different (PT, MW and HA) drying procedures

The tablets were pressed with 10 t for 1 min. Crystallinity was determined and calculated using a Bruker D2 Phaser software – DIFFRAC.EVA V6.0.

3. Results and Discussion

Herein we examine the capacity of two characterisation techniques, frequently used in materials examination, i.e. TGA and XRD, to assess structural changes during the drying phase in laundry care. For this purpose, we used fabrics based on natural, synthetic fibres, as well as their blends (i.e. 100% cotton, PES/cotton (65/35), 100% PES, viscose, wool, silk, polyacrylonitrile (PAN) and polyamide (PA6.6). The samples were exposed to different drying methods, namely: photothermal (PT), microwave (MW) and hot air (HA) drying.

TGA thermograms of the 100% CO fabric demonstrate the initial mass loss in the 50–150 °C thermal regions related to the evaporation and removal of adsorbed water. From Fig.1 (top-right), where differently (PT, MW and HA) dried samples before and after 25 soaking/drying cycles are presented, it can be seen that air dried sample has the highest mass loss in mentioned region, indicating a higher presence of adsorbed water. The following temperature region (after 300 °C) is associated to depolymerisation, cleavage of C-O and C-C bonds, and opening of the glucose ring, where the maximum thermal decomposition occurs. For the same sample, a slight change in decay rate is seen. At ~ 400°C, the analysed samples are in the ″carbonised″ state, and in this segment, there are no visible differences between the remaining mass, which is ~ 12% for all samples, irrespective of type of drying.

The wool sample (Fig.1, middle-left) shows the typical temperature behaviour of protein-based (keratin) material. The initial region of the thermogram (up to ~150°C) represents the region of water evaporation, where changes occur in the amorphous regions of the protein chains due to water migration. Then (between 230°C and 250°C) follows the process of

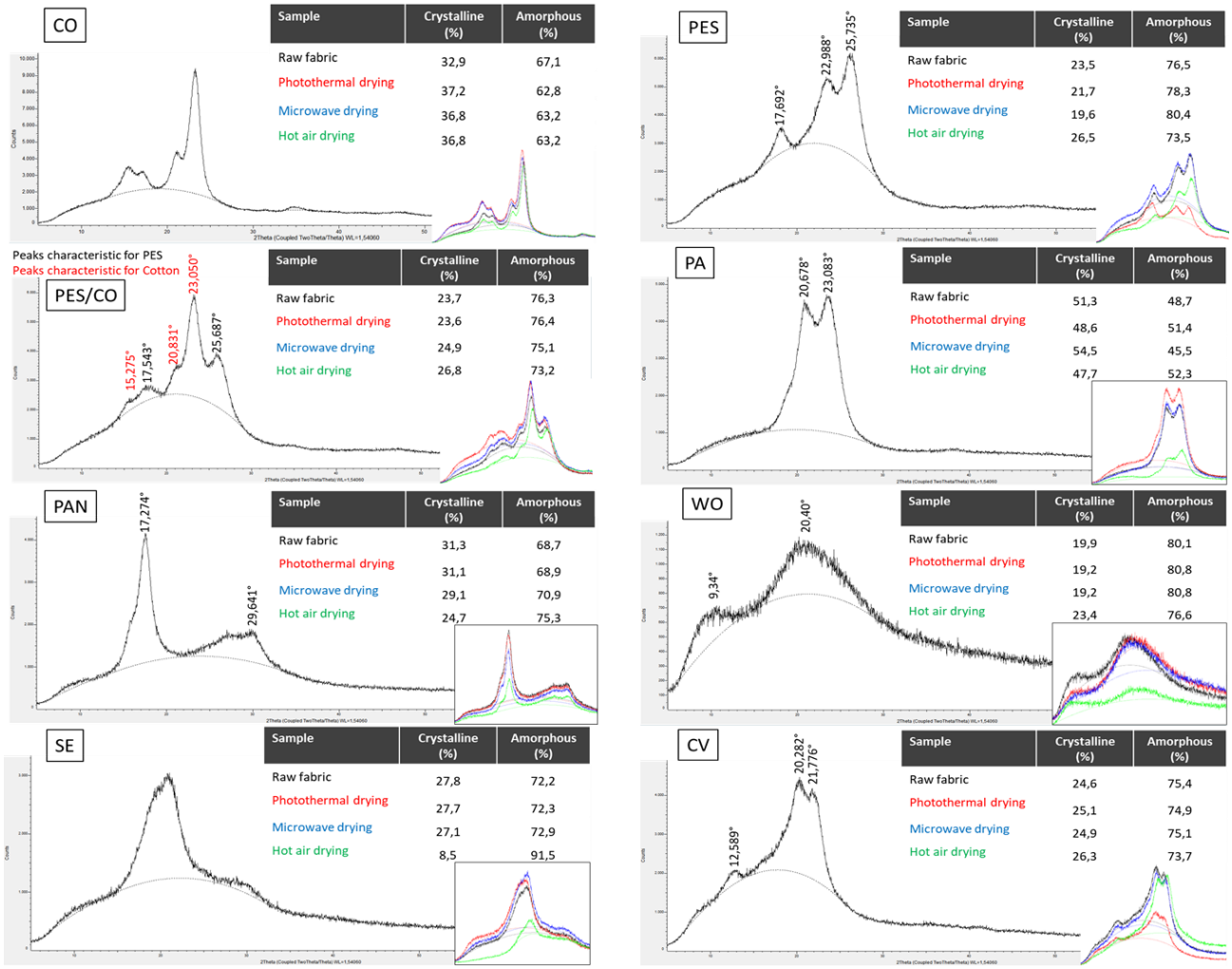

Fig.2 XRD spectra of all samples (abbreviations of samples are on the top left side of the spectra), cut of XRD spectra of samples with combined drying procedures (bottom-right of the spectra) and proportion of crystalline and amorphous region (top-right of the spectra)

temperature degradation of the lateral chains of keratin, which are part of α helices. Final degradation starts at ~400°C. As can be seen, the profile of all curves is very similar between the samples treated 25x, while the reference sample is slightly more stable, and its thermal degradation starts slightly later and is more separated from the evaporation area.

The most noticeable difference is seen in the viscous sample (Figure 1, bottom-right), especially in the region of temperature decay, where depolymerisation, cleavage of C-O and C-C bonds, and opening of the glucose ring occur. Interestingly, the control sample, which was not exposed to 25 cycles of soaking drying, regardless of the type of drying, has lower thermal stability, and thermal degradation begins and continues after the water evaporation (at ~ 200 °C) is complete. All other samples, which were exposed to 25 cycles of different drying/soaking, do not differ from each other, except for % mass loss, with the carbon residue being the largest in the sample dried in a microwave dryer.

In the case of the silk sample (data not presented), the temperature behaviour is similar, except for the HA sample, in which the degradation of the sample starts earlier and has ~33% of the remaining mass at 400°C, which is ~10% less than the other samples.

The thermal behaviour of the PES/cotton (65/35) MW and HA samples differs slightly from the control in that their decomposition starts earlier, and at the final temperature (400 °C), the carbon residue is equal (~8%). In the case of synthetic samples PA 6.6 (Fig.1, bottom), 100% PES, and PAN (data not presented), there are no visible differences, which results from their high thermal stability in the temperature range of the analysis (up to 400 °C).

Data from XRD analysis (Fig.2) were used to determine the changes at the macromolecular level of fibres, mainly their arranged crystalline, and dis-ordered amorphous regions. The ratio between these regions can

give some information regarding the structural damages in the textile material, occurring during the household tumble drying. The XRD spectra for individual standard fabrics processed as raw (non-treated) and treated with 3 different drying procedures (photothermal, microwave, hot air), and calculated proportions of crystalline and amorphous regions detected in each sample, together with corresponding XRD spectra are presented in Fig.2. From the results it can be seen that in all samples regardless of their fibre composition we can observe that the photothermal and microwave drying process did not signify-cantly influence the ratio between crystalline and amorphous domains in the fibres. But the application of hot air drying, performed at 80°C, did show crystalline/amorphous ratio changes above the standard deviation, calculated from the raw, photothermal and microwave values, presented in Tab.2. In case of PES/CO, PAN, WO, SE, and CV the changes in crystallinity are detected, while in the case of PA and CO samples the value of crystallinity is in the area of standard deviation. It was also expected that the drying process using hot air would not influence the highly crystalline structure characteristic for PA fibres (51.3%), as well as cotton sample (32.9%) resistant to heat at 80°C due to its cellulose crystalline structure. The major change in crystallinity was observed in wool and silk samples, known as materials with low resistance to high heat treatments. In case of wool, the the increase in crystallinity can be observed, which can be attributed due to the shrinkage and felting of wool fibres during the wetting. In silk sample the drastic decrease in crystallinity from 27.8% in the case of raw sample, to 8.5% in the case of hot air dried sample can be observed. Silk and wool fibres are known for their high water and moisture absorbency and shrinking ability and therefore obtained results were expected.

5. Conclusion

According to the results obtained during the study, we can conclude that the TGA and XRD methods show potential in the case of predicting the structural changes appearing in the tumble drying process of textile materials. TGA analysis enables the identification of differences between natural fibre samples, including viscose, before and after 25 cycles of wetting/drying using different drying techniques. In the case of synthetic samples, the differences are not visible, which indicates that no changes have occurred or that the resulting changes do not affect the thermal behaviour of the samples. While in the case of XRD analysis, we showed that the method has potential for the detection of small changes in the crystalline structure of fibres upon drying process.

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Table 2: Crystallinity values of samples measured and calculated with XRD method

Sample	Crystallinity (%)				
	Raw	PT	MW	StDev	HA
CO	32.9	37.2	36.8	2.38	36.8
PES/CO	23.7	23.6	24.9	0.72	*26.8*
PES	23.5	21.7	19.6	1.95	*26.5*
PA	51.3	48.6	54.5	2.95	47.7
PAN	31.3	31.1	29.1	1.22	*24.7*
WO	19.9	19.2	19.2	0.4	*23.4*
SE	27.8	27.7	27.1	0.38	*8.5*
CV	24.6	25.1	24.9	0.25	*26.3*

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