

How to measure the angle of repose of hazardous substances in the test centres for dangerous goods packagings

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Abstract

The flow properties of powdery or granular filling substances for dangerous goods packagings are safety-relevant parameters. To specify the flow behaviour, the angle of repose is measured in the recognized test centres for dangerous goods packagings in Germany. Previous investigations performed on non-hazardous substances revealed that some of the methods currently used have disadvantages in application. Additionally, for occupational health and safety reasons, it was generally viewed critically to carry out measurements of the angle of repose for dangerous goods at all. Instead, the dimensionless Hausner ratio to describe the flow behaviour was proposed. In this work, the investigations were extended to real hazardous substances to concretize the assessment. Five exemplary hazardous substances were tested for their angle of repose using the methods commonly applied in the test centres. The Hausner ratio was also determined. In addition, the influence of a different climatic preconditioning on the angle of repose measurement was examined using three selected non-hazardous bulk materials. The results show that the measurement of the angle of repose is not fundamentally excluded for dangerous goods. However, for reasons of applicability, repeatability and occupational health and safety, only the ISO method can be applied for dangerous filling substances. This method provides conservative results regarding a safety-related evaluation of flow properties for the transport of dangerous goods. In principle, both the ISO method and the determination of the Hausner ratio can be used for dangerous goods. It is also essential especially with finely powdered filling goods, to carry out controlled preconditioning.

KEYWORDS

angle of repose, flow properties, flowability, Hausner ratio, powders, sift-proofness

1 | INTRODUCTION

For many types of packaging containing bulk solids (e.g. powdery or granular food, pharmaceuticals, fertilizers, building materials or chemicals), the flow properties of the filling goods are an important parameter for filling the packaging, its behaviour during transport and for

emptying.¹ In the special case of dangerous goods packagings, the flow properties of the filling substance are also important for safety reasons.

According to the UN Model Regulations (UN 6.1.5.2.1),² substances to be transported in dangerous goods packagings may be replaced by other substances during the design type tests as long as

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this does not invalidate the test results. For solids, this substance must have the same physical properties (mass, grain size) as the substance to be carried. The physical properties of the replacement filling substance have to be documented in the test report.

For German approvals for packagings for solid dangerous goods, the minimum angle of repose of the filling substances for which the packaging may be used must also be specified in the test report and in the certificate of approval. Here, the angle of repose acts as a parameter to describe the flow properties of the solid filling material. The user has to make sure that only those filling goods are transported in the approved packaging whose angle of repose is higher than the angle of repose specified in the approval. The higher the angle of repose of a bulk material, the worse its flow properties. The flow properties of bulk materials affect two aspects, namely both the mechanical safety of the packaging and the safety against the release of substances under normal conditions of carriage.^{1–3}

In the first case (mechanical safety), flow phenomena are responsible for the tearing of a bag due to impact. The poorer the flowability of the bulk material, the lower the damaging effect on the packaging wall.⁴ Depending on the bulk solid, part of the vertical load is deflected horizontally on impact. The resulting horizontal flow stresses the packaging wall as the particle mass decelerates, which can lead to failure.⁵ By examining the impact processes using shock recording and high-speed cameras, Kaltenborn⁵ describes in detail the processes that take place within the bulk material of a flexible packaging after the shock. Four phases can be distinguished during the impact process: When the underside of the packaging hits the impact plate, compression begins, and the particles of the filling material compact quickly. By decelerating the movement of the particles, the measured force increases in the vertical direction up to a first maximum (phase 1). In the middle of the packaging, the particles only move vertically during the entire impact. Depending on the flow properties of the bulk solid and the elasticity of the packaging material, the particles are deflected horizontally in the edge zones. The originally vertical movement receives a horizontal component. The horizontal deflection of the particles reduces the proportion of vertical deceleration; the measured force decreases (phase 2). As the process progresses, the horizontal compensating movement of the particles is increasingly restricted by the flexible body of the packaging. The vertical force increases to a second maximum as the particle motion slows down. At this point, the packaging body is maximally deformed, and the packaging is decelerated to a standstill. The compression is finished (phase 3). Now, the deformed body of the packaging releases its energy again and contracts. The direction of movement of the particles is upwards. This reduces the force until the end of the impact process. The packaging rebounds, partially lifts off and settles until it comes to rest (phase 4). In general, a good flowability of the filling material, expressed by a low angle of repose or a low Hausner ratio, suggests that this leads to a greater damage effect and therefore to a reduction in safety,^{4,6} because the horizontal flow phenomena in the edge zones are responsible for the failure of the packaging after the impact.⁴ However, there are bulk solids with different behaviour in the drop test for which this general relationship does not apply.⁵ In addition to

the flowability, the horizontally deflected force from the vertical direction is also decisive for the stress on the packaging.⁵ If it is a bulk material with high elasticity of the individual particles, a vertical load during shock leads to deformation and expansion in the transverse direction, which leads to higher horizontal impacts. This effect means that PP granules examined in drop tests are more damaging to the packaging than salt, which consists of inelastic particles, although both have similar angles of repose.⁵ However, the extent of the force deflection on impact is not taken into account by the angle of repose.

In the second case (safety against the release of particles), weak points in the packaging play a role (joints, closures, micro-perforations), but also material properties of the filling substance, for example the flowability of the bulk material. Powder with good flowability can escape from insufficiently pasted joints already during manual filling.³ There have been several reports of repeated leaks of dangerous goods from bags and FIBC that are actually intact in practice.^{1,3,7,8} The following figures show releases that were detected by the German Police North Rhine-Westphalia Münster police during their controls in 2022.

In Figures 1–2, the release of an environmentally hazardous substance (copper sulphate, UN 3077) from the stitched join of a paper bag 5M2 (paper bag, multi-wall, water resistant) is visible. Figure 3 shows the release of another UN 3077 substance (application in nutrition industry) from the stitched join of a paper bag 5M2. In Figure 4, potassium nitrate (UN 1486) escapes from the micro-perforations of a 5H4 plastics film bag. Figures 5–6 display the release of a toxic inorganic substance (UN 3288) from the insufficiently closed closure of a 13H3 plastics FIBC (woven plastics with liner). Figure 6 shows that a heap of bulk material is forming under the loading unit as a result of the escape of particles.

These releases result from a combination of different influencing factors, as explained in Schlick-Hasper et al.³ In all cases, the leaking of particles occurs from critical components of intact bags or FIBC (joints, micro-perforations and closures). However, the properties of the respective filling substance also play a role (in particular particle size and flow properties).

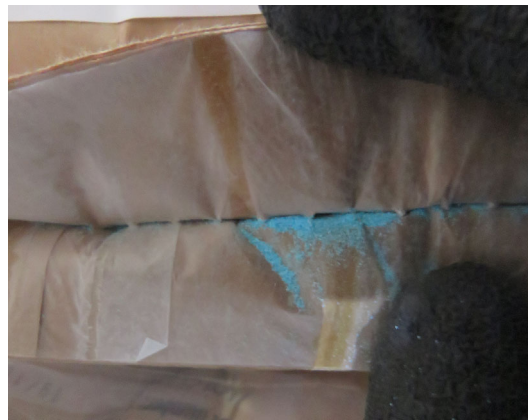


FIGURE 1 Release of an environmentally hazardous substance (UN 3077) from the stitched join of a 5M2 paper bag (Police North Rhine-Westphalia Münster).



FIGURE 2 Release of an environmentally hazardous substance (UN 3077) from the stitched join of a 5M2 paper bag (Police North Rhine-Westphalia Münster).



FIGURE 3 Release of an environmentally hazardous substance (UN 3077) from the stitched join of a 5M2 paper bag (Police North Rhine-Westphalia Münster).

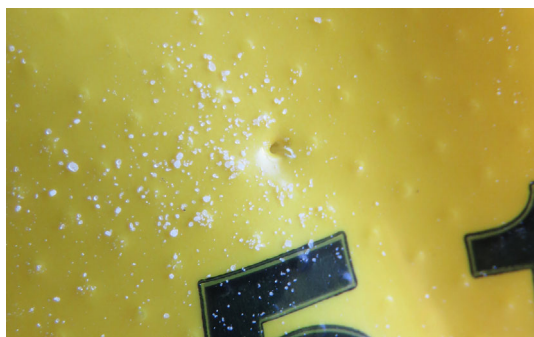


FIGURE 4 Release of an oxidizing substance (UN 1486) from the micro-perforations of a 5H4 plastics film bag (Police North Rhine-Westphalia Münster).

In addition to the specification of other material parameters of the filling substance, the characterization of the flow properties is therefore particularly important in practice when transporting dangerous goods, both with regard to mechanical safety and sift-proofness.¹



FIGURE 5 Release of toxic substance (UN 3288) from the closure of a 13H3 woven plastics FIBC (Police North Rhine-Westphalia Münster).



FIGURE 6 Release of toxic substance (UN 3288) from the closure of a 13H3 woven plastics FIBC (Police North Rhine-Westphalia Münster).

The problem is that different methods are currently applied for measuring the angle of repose in the recognized test labs for dangerous goods packagings in Germany, as no specific method is prescribed.³ The certificate of approval does not state which measurement method was used to determine the angle of repose and how the samples were preconditioned. It is difficult to assess how the value was determined.

This was the motivation for part 1 of research on the subject.¹ In a first step, experimental investigations of the angle of repose were carried out using four methods commonly applied in the test centres on 12 non-hazardous powdery or granular bulk solids. The findings are that the results for the angle of repose obtained with the different methods deviate significantly from one another or have poor repeatability in some cases. The so-called funnel test systematically delivered too small results for the angle of repose for comparatively coarse-grained filling goods. It was suggested that the dimensionless Hausner ratio could be used to specify the flow properties instead of the angle of repose. However, practical experience in handling dangerous goods using the methods was not yet available. The investigations were only carried out on non-hazardous goods and after preconditioning in a uniform standard climate (atmosphere having a

controlled temperature of $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and controlled relative humidity (r.h.) of $50\% \pm 2\%$ r.h. (UN 6.1.5.2.3).

The objective of this study is therefore to evaluate the applicability of the methods for measuring the angle of repose when testing substances with hazardous properties and to investigate the influence of different climatic preconditioning. For this, the resulting moisture content of the filling substance has to be determined. Since this involves drying the substance by heating it to a temperature of 105°C ⁹ and some of the five hazardous substances examined tend to thermally decompose at temperatures above 30°C (ammonium bicarbonate) or a maximum storage temperature of 40°C (Biathlon 4D, Pergafast) or 30°C (Cantus) is specified, a determination of the moisture content cannot be performed on these. Therefore, for these five substances, the preconditioning and subsequent measurement of the angle of repose was carried out solely in the preferred standard climate according to UN Model Regulations. Instead, the effect of different climatic preconditioning, and thus, a different moisture content was examined on three non-hazardous substances (chrome ore sand, Eskal 10, Eskal 0.5–1.0). In addition to the UN standard climate previously used, conditioning at a temperature of 23°C and 10% r.h. was also applied, as well as at 23°C and 90% r.h.

As in the first part of the investigations,¹ the four methods are evaluated for their repeatability, their applicability to certain types of solid filling goods and their suitability regarding occupational health and safety. The dimensionless Hausner ratio (quotient of tapped density and aerated bulk density) is again determined as an alternative parameter for characterizing the flow properties. The additional focus here is in particular on the assessment of the suitability for the handling of dangerous goods and an assessment with regard to safety when transporting dangerous goods. The results are therefore important for testing practice in the recognized testing centres for dangerous goods packagings, but also for manufacturers of hazardous bulk solids and the subsequent users of the packaging.

2 | DEFINITIONS

The theoretical background of the flow properties of bulk solids has already been described in detail in the first part of the investigations.¹ At this point, therefore, only a summary of the most important correlations is given. The parameters presented below, angle of repose and Hausner ratio, are simple and quick methods of determining flowability to compare different materials.¹⁰ Also in the pharmaceutical industry, the determination of the angle of repose and the Hausner ratio are among the most common methods for characterizing the flow properties of powders and bulk solids.¹¹

2.1 | Angle of repose

The angle of repose α is defined as the angle of inclination of the free surface to the horizontal of a bulk solid heap.¹² For a conical heap, the

angle of repose is the angle between the conical slope of a pile of solid materials and the horizontal base.^{11,13,14}

The steeper the angle of repose, the higher the cohesiveness of a bulk solid; the lower the angle of repose, the more fluid-like and free-flowing the bulk solid.^{13,14} There are various classifications in the form of reference tables for characterizing the flowability using the angle of repose. According to Carr,¹⁴ the angle of repose is a direct indication of the potential flowability of dry solids, as shown in Table 1. This original classification of Carr is widely used in practice.

Kalman¹⁰ comprehensively summarizes the current state of research on the subject of the dependence of the angle of repose on the moisture content. He evaluates the measurements of various authors and own measurements and summarizes that the bulk materials examined can generally be divided into three categories according to their response to moisture content: solid particles (defined as particles that do not contain any internal pores, category I), for example glass beads or sand; porous particles (category II), for example pulverized carbon or zeolites; and particles that change size depending on the moisture content (category III), for example wheat grain or rice.

The three non-hazardous substances examined in this work can be assigned to category I. In these materials, the particles hold all of their moisture on their outer surface, and the moisture content is shared between points of contact of the particles, creating liquid bridge forces. If the moisture content is increased starting from a moisture content of zero, the angle of repose first increases until a maximum is reached (zone I) and then moderately decreases (zone II).

The behaviour of the decreasing flowability (increasing angle of repose) in zone I is caused by the increase of liquid bridge forces for each individual particle as the moisture content increases. As the moisture content is further increased (zone II), the influence of liquid bridging forces between individual particles becomes less dominant as the individual particles begin to form agglomerates. An increased size of agglomerates favours better flowability of the substance, which leads to decreasing angles of repose. As the particle size is reduced, the maximum angle of repose becomes higher. Finer powders can contain more moisture content compared to large particles because they have more contact points. The phenomena just described occur for both spherical and non-spherical solid particles.¹⁰

The relationship between internal friction and wall friction with respect to the surface of the base plate dictates the heap shape.

TABLE 1 Classification of flow behaviour of solids based on the angle of repose according to Carr.¹⁴

Angle of repose [°]	Denomination
25–30	Excellent
31–35	Good
36–40	Fair
41–45	Passable
46–55	Poor
56–65	Very poor
> 66	Very, very poor

Heaps can be conical with straight slopes, whether symmetrical or not. Further, the heaps can be concave (for low wall frictions and high internal frictions) or convex (for high wall frictions and low internal frictions).¹²

2.2 | Hausner ratio

The Hausner ratio is determined from the measured values of the tapped bulk density ρ_t and the aerated bulk density ρ_a of a powdery or granular substance^{11,15-17}:

$$H = \frac{\rho_t}{\rho_a} \quad (1)$$

Easily flowing bulk solids tend to have a low Hausner ratio. In the case of less flowable substances, there are significantly higher interactions between the particles and the Hausner ratio is higher. In particular, the cohesive forces are higher.^{11,12} The generally recognized classification of the flow behaviour of dry solids according to Carr¹⁴ is shown in Table 2.^{11,12,17-20}

3 | MATERIALS

3.1 | Non-hazardous substances

3.1.1 | Characterization of particle size

Three non-hazardous bulk solids were examined for their angle of repose after they had been subjected to different types of climatic preconditioning.

TABLE 2 Classification of flow behaviour of solids based on the Hausner ratio according to Carr.¹⁴

H [–]	Flow behaviour
1.00–1.11	Excellent
1.12–1.18	Good
1.19–1.25	Fair
1.26–1.34	Passable
1.35–1.45	Poor
1.46–1.59	Very poor
>1.60	Very, very poor

TABLE 3 Parameters for the characterization of the particle size of the three non-hazardous bulk solids (¹).

Substance name	CAS no.	$x_{mod,3}$ [μm] (mode)	$x_{min,3}$ [μm]	$x_{10,3}$ [μm]	$x_{50,3}$ [μm] (median)	$x_{90,3}$ [μm]	$x_{max,3}$ [μm]	Span [–]
Chrome ore sand	1308-312	330.0	74.0	158.7	274.0	442.0	1030.0	1.03
Eskal 10 ^a	1317-65-3	11.2	0.2	4.6	11.5	20.2	75.3	1.35
Eskal 0.5–1.0	1317-65-3	942.3	123.3	580.7	785.0	1015.7	1122.3	0.55

^aEskal 10 contains a flow agent, 0.25% calcium stearate (by weight).

Chrome ore sand (>46% Cr₂O₃, >25% FeO, >15% Al₂O₃) was obtained from Mineralwerk Hamm GmbH, Hamm, Germany. The Eskal powder (Eskal 10) and the Eskal grained type (Eskal 0.5–1.0) consist of natural calcium carbonate CaCO₃ (>99.10%) and were obtained from KSL staubtechnik GmbH, Lauringen, Germany.

Table 3 lists parameters for the particle size characterization of the three non-hazardous substances obtained from measuring the particle size distribution. The explanation of the parameters and the measured values for these quantities are listed in the first part of the investigations.¹

3.1.2 | Measurement of moisture content

The moisture content of the three non-hazardous bulk materials was determined according to DIN EN ISO 17982-1⁹ after they had been preconditioned for at least 4 days in three different climates. This involves drying the samples at a temperature of 105°C. The moisture content X is defined as the ratio of the water mass m_w to dry solids mass m_d ²¹:

$$X = \frac{m_w}{m_d} \quad (2)$$

Table 4 summarizes the results for moisture content, also shown in Figure 7.

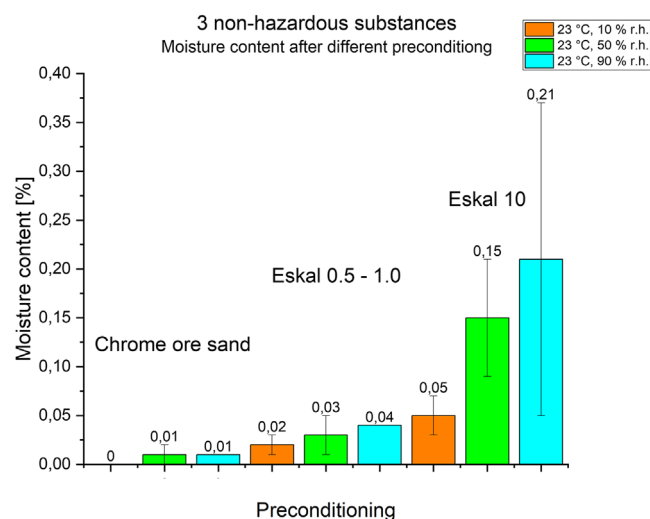
For each substance, a statistical analysis of the moisture content was performed by analysis of variance (one-way ANOVA and Kruskal–Wallis test) to evaluate the effect of the different preconditioning. The type of preconditioning (different relative air humidity) forms the influencing variable (factor), each preconditioning type is considered as group. The moisture content is the dependent variable. The selected null hypothesis H_0 states that there is no difference between the mean values of the individual groups. The alternative hypothesis H_A is that at least two groups have significant differences in their expected values. The significance level is set at 0.05.

For chrome ore sand, the null hypothesis was accepted. A change in the relative humidity of the preconditioning has no statistically significant effect on the moisture content. The maximum moisture content in the bulk solid is 0.01%.

For Eskal 0.5–1.0, an increase in moisture content from 0.02% to 0.04% is observed. The null hypothesis was rejected, so there is a statistically significant influence of the relative humidity on the moisture content in the bulk material for this substance. Nevertheless, an increase in the relative humidity during preconditioning from 10% to

TABLE 4 Moisture content of the three non-hazardous bulk materials after different preconditioning.

Substance name	Climatic preconditioning					
	23°C, 10% r.h.		23°C, 50% r.h.		23°C, 90% r.h.	
	X [%]	σ [%]	X [%]	σ [%]	X [%]	σ [%]
Chrome ore sand	0.00	0.00	0.01	0.01	0.01	0.00
Eskal 10	0.05	0.02	0.15	0.06	0.21	0.16
Eskal 0.5–1.0	0.02	0.01	0.03	0.02	0.04	0.00

**FIGURE 7** Moisture content of the three non-hazardous bulk materials after different preconditioning.

50% to 90% only has a minor effect on the resulting moisture content of the bulk material.

The moisture content determined is highest for Eskal 10, the most fine-grained of the three substances examined. After preconditioning in the humid climate (23°C, 90% r.h.), the moisture content of the bulk solid is 0.21%. The null hypothesis was also rejected for this substance, so there is a statistically significant influence of preconditioning on bulk moisture content. The direct comparison with Eskal 0.5–1.0 (a coarser fraction of the same substance [calcium carbonate]) confirms the theory that finer powders are able to absorb a higher amount of moisture¹⁰ (see Section 2.1).

The handling of Eskal 10 is associated with a high level of dust generation.¹ For this reason, when all three substances were pre-stored in the respective climate, the respective substance was not stirred to achieve homogenization of the moisture content within the pre-stored substance. It can therefore not be ruled out that there is a local uneven distribution of moisture within the bulk material, which explains the high scatter, especially with Eskal 10. However, this procedure was chosen in order to achieve comparability with preconditioning of dangerous goods. In the case of dangerous goods, it is also not recommended to stir the respective substance during climatic preconditioning for occupational safety reasons.

3.2 | Hazardous substances

3.2.1 | Characterization of particle size

Five hazardous bulk solids were examined for their angle of repose and Hausner ratio after conditioning in standard climate at 23°C and 50% relative humidity. Three of these substances are classified as dangerous goods.

Sodium nitrate, ammonium bicarbonate, Biathlon 4D and Cantus were obtained from BASF SE, Ludwigshafen, Germany. Pergafast™ 201 was obtained from Solenis Germany GmbH & Co. KG, Krefeld, Germany.

Sodium nitrate HQ free flowing (non-food grade) is a white, crystalline, water-soluble, hygroscopic powder that contains an anti-caking agent. It is a raw material and a process chemical, for example for the agricultural industry. According to dangerous goods legislation, it is classified as a substance of class 5.1 (Oxidizing substances), packing group III (substances presenting low danger), UN No. 1498 (sodium nitrate).

Ammonium bicarbonate O Food Grade is a white, crystalline, water-soluble, hygroscopic powder. It is used as food additive in baking industry, raw material and process chemical. Thermal decomposition is to be expected at temperatures above 30°C, which is why the substance must not be heated.

Biathlon 4D is a beige, water-dispersible (non-water-soluble) granulate. It is a crop protection product and herbicide. It is classified as a dangerous substance of class 9 (miscellaneous dangerous substances and articles), packing group III (substances presenting low danger), UN No. 3077 (environmentally hazardous substance). Exceeding a temperature of 40°C is to be avoided for this product.

Cantus is a grey-brown, water-dispersible (non-water-soluble) fine granulate. It is used as a crop protection agent and fungicide. This substance should be protected from exceeding a temperature of 30°C.

Pergafast™ 201 is a sulfonylurea derivate. Its physical form is a white powder that is insoluble in water. It is a colour developer for thermal paper production. It is classified as a substance of class 9 (miscellaneous dangerous substances and articles), packing group III (substances presenting low danger), UN No. 3077 (environmentally hazardous substance). The maximum storage temperature of this product is 40°C.

The measurements of the particle size distribution of the hazardous substances were carried out by Sympatec GmbH,

Clausthal-Zellerfeld, Germany. Three sub-samples of each substance were measured. Table 5 shows the results. See Schlick-Hasper et al.¹ for the explanation of the listed parameters.

Two different systems were used for the dispersion: dry dispersion (RODOS/L [526 F]) for ammonium bicarbonate, Cantus and Pergafast and gravity dispersion (GRADIS 526 F) for sodium nitrate and Biathlon 4D.

For all five substances, laser diffraction analysis was applied using the HELOS (Hi202) system. For sodium nitrate, ammonium bicarbonate and Biathlon 4D, the measuring range R7 (0.5/18.0–3500 μm) was used. For Cantus, the measuring range R6 (0.5/9.0–1750 μm) was used. For Pergafast, the measuring ranges R2 and R6 were combined (0.25/0.45–1750 μm).

For reasons of simplification, the full brand names are not given for the designation of these five substances in the further text, but only short names. A comparison of the characteristic values shows that Pergafast is the most fine-grained substance ($x_{50,3} \approx 117 \mu\text{m}$). The two coarsest substances are sodium nitrate and Biathlon 4D ($x_{50,3} \approx 610 \mu\text{m}$ and $x_{50,3} \approx 625 \mu\text{m}$). In the case of Pergafast, there is a bimodal particle size distribution.

4 | METHODS

4.1 | Preconditioning of the powdery and granular substances

4.1.1 | Hazardous substances

Before the tests (measurement of the angle of repose and the Hausner ratio) are performed, the bulk solids are conditioned for at least 120 h in an atmosphere having a controlled temperature of $23^\circ\text{C} \pm 2^\circ\text{C}$ and a relative humidity of $50\% \pm 2\%$ according to UN 6.1.5.2.3.² Most test centres for dangerous goods packagings, especially those for packaging made of paper and fibreboard, can implement this standard climate. According to UN 6.1.5.2.3, at least 48 h are prescribed for preconditioning. After preconditioning, the sample quantity required to carry out a single test is taken and subjected to

the measurements (results; see Sections 5.2 and 5.3) within 1 min under a fume cupboard. Since ammonium bicarbonate is slightly hygroscopic and tends to form agglomerates (see Figure 8), the substance had to be sieved before starting the preconditioning. The flow properties of bulk solids are also influenced by their chemical composition.²² Substances with hygroscopic properties actively attract and retain water from the environment, making them extremely sensitive to moisture. In the case of ammonium bicarbonate, this manifests itself in the formation of agglomerates. It could not have been used in subsequent tests without prior sieving. However, no statement can be made as to the extent to which the flow properties of ammonium bicarbonate and the other hazardous substances change with the moisture content, as this could not be tested: A variation of the climate for the preconditioning and a determination of the moisture content of the hazardous substances was not carried out, since the majority of the substances must not be heated to a temperature of more than 30 or 40°C (see Section 3.2.1).

4.1.2 | Non-hazardous substances

The three non-hazardous substances were also preconditioned in a drier climate ($23^\circ\text{C} \pm 2^\circ\text{C}$, $10\% \pm 2\%$) and in a climate with higher relative humidity ($23^\circ\text{C} \pm 2^\circ\text{C}$, $90\% \pm 2\%$) in addition to the standard climate. The moisture content after preconditioning is determined for

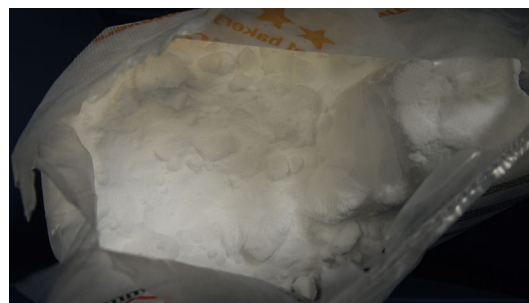


FIGURE 8 Formation of agglomerates in the slightly hygroscopic ammonium bicarbonate.

TABLE 5 Parameters for the characterization of the particle size of the five hazardous bulk solids (Sympatec GmbH, Clausthal-Zellerfeld, Germany).

Substance name	CAS no. /class, packing group, UN-no.	$x_{mod,3}$ [μm] (mode)	$x_{min,3}$ [μm]	$x_{10,3}$ [μm]	$x_{50,3}$ [μm] (median)	$x_{90,3}$ [μm]	$x_{max,3}$ [μm]	Span [–]
Sodium nitrate HQ free flowing (non-food grade) ^a	7631-99-4, 5.1-III, UN 1498	786.9	74.0	265.9	609.9	990.69	1740.0	1.19
Ammonium bicarbonate O Food Grade	1066-33-7	458.3	26.0	191.86	420.15	682.95	1220.0	1.17
Biathlon 4D	142469-14-5	657.3	120.0	430.52	624.59	862.92	1460.0	0.69
Cantus	188425-85-6	217.6	37.0	104.07	194.63	328.73	610.0	1.15
Pergafast™ 201	232938-43-1, 9-III, UN 3077	3.4; 418.4	0.3	2.45	116.68	507.54	418.4	4.35

^aSodium nitrate contains an anti-caking agent.

each material according to DIN EN ISO 17892-1⁹ on different portions of the laboratory sample (results; see Section 3.1.2). After pre-conditioning, the sample quantity required to carry out a single test is taken and subjected to the measurements (results; see Section 5.1) within 1 min under a fume cupboard.

4.2 | Measurement methods for the angle of repose

The description of the methods used, which are currently common procedures in the recognized test centres for dangerous goods packaging in Germany, is given in detail in the first part of the investigations.¹ At this point, therefore, only the most important points of the respective procedures are discussed.

4.2.1 | Method according to ISO 4324

The experimental setup for this method is shown in Figures 9 and 10.^{23,24}

A sample of 150 mL of the bulk material is placed in the glass funnel, and the closure is opened. The substance is released through the funnel outlet to flow and form a conical pile of material on the circular base plate made of transparent plastic, having a fixed diameter of 100 mm. The use of the agitator is optional. Excess powder will fall laterally from the base plate. The height of the powder cone is



FIGURE 9 Method according to ISO 4324—Biathlon 4D during the discharge process from the funnel.

measured using a slewable measuring bar. The angle of repose is calculated from this measured height h of the pile and the fixed diameter of the circular base plate^{23–25}:

$$\tan \alpha = \frac{2h}{100} = \frac{h}{50} \quad (3)$$

A minimum of five tests are carried out for each material. Stirring with the agitator was used for the following substances to facilitate their flow out of the funnel: sodium nitrate, ammonium bicarbonate and Pergafast.

Since the angle of repose is calculated with this method from a measurement of the height and the base diameter assuming a perfect conical shape, the value determined in this way represents an average value.¹² To ensure comparability, it was intended to also determine the average angle of the slope for the other methods, in which the angle of repose was measured manually with an inclinometer.

4.2.2 | ‘Funnel test’—Test method used in the test labs for dangerous goods packagings in Germany

The experimental setup is displayed in Figure 11.



FIGURE 10 Method according to ISO 4324—Measurement of the height of powder cone using the slewable measuring bar (Biathlon 4D).

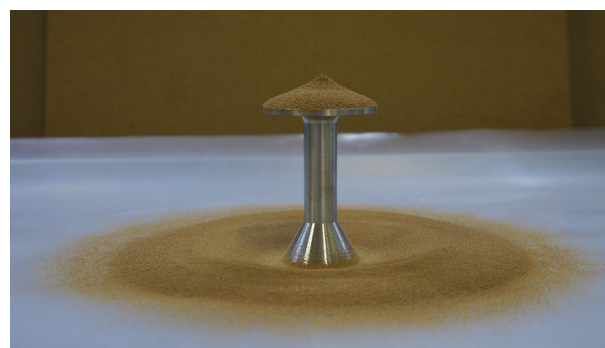


FIGURE 11 ‘Funnel test’: Test setup—Cantus.

The equipment consists of a stainless steel stamp whose circular platform has a diameter of 50 mm. The outlet diameter of the plastic funnel is 30 mm. The funnel is placed with its outlet opening on the test stamp and is filled with 100 mL of the powdery or granular substance. The funnel is then fixed with both hands in the centre of the test stamp and slowly pulled upwards until the bulk material runs out and forms a cone-shaped heap on the platform. Excess particles are allowed to drain away past the circumference of the platform. The angle of repose of the heap is measured by using an inclinometer (Angle Star DP-45 Digital Protractor, MEAS Deutschland GmbH, Dortmund, Germany). Two values are determined for each pile (right and left slope). At least five experiments are conducted on each substance.¹

4.2.3 | 'Plate method'—Test method used in the test labs for dangerous goods packagings

This method is used in two variants. The geometry of the test setup is the same, but the material of the plates is either plexiglass (Figure 12) or mineral glass.

The inside dimensions of the container are 940-mm length, 220-mm height and 30-mm distance between the plates. The plastic funnel has an outlet diameter of 20 mm, and the height of the funnel outlet above the rectangular base area of the test setup is 220 mm. 1.5 L of the bulk sample is placed in the funnel, and the outlet is opened. The bulk material is released through the funnel outlet to flow and form a pile between the plates. The angle of repose of the heap is measured by applying an inclinometer (Leica Disto D3a, Leica Geosystems AG, Heerbrugg, Switzerland). Two values are determined for each pile (right and left slope). At least five heaps are formed for each substance.¹

4.3 | Determination of the Hausner ratio

The Hausner ratio is calculated from the measured values of the aerated bulk density and the tapped density (Equation 1). The aerated

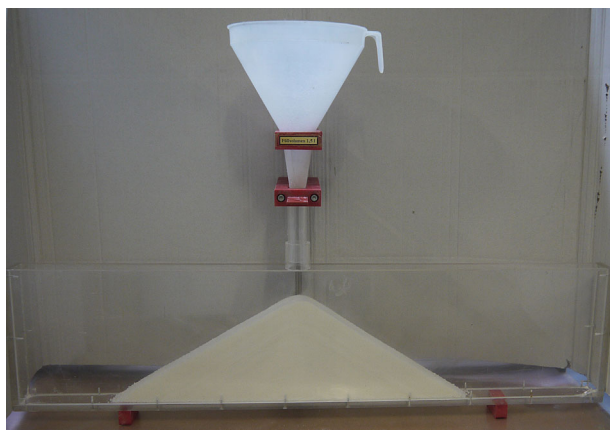


FIGURE 12 'Plate method' (plexiglass): Test setup—sodium nitrate.

bulk density is measured in accordance with DIN EN ISO 60.²⁶ The measurement is repeated six times for each material. For the measurement of the tapped density, a tamping volumeter according to DIN EN ISO 787-11²⁷ is used (Stampfvolumeter STAV II, J. Engelsmann AG, Ludwigshafen, Germany). The sample is subjected to 1250 tamping cycles. Six tests are carried out on each material.

5 | RESULTS

5.1 | Angle of repose—Non-hazardous substances (different climates for preconditioning)

The mean angle of repose $\bar{\alpha}$, the standard deviation σ and the coefficient of variation c_v per substance and method are listed in Table 6 (dry climate), Table 7 (standard climate) and Table 8 (humid climate). Figures 13–15 display the results for chrome ore sand, Eskal 0.5–1.0 and Eskal 10.

When comparing the results of the four measurement methods for chrome ore sand (Figure 13), there is no systematic influence of preconditioning. The results per method for the three different climates agree well. This is plausible because the moisture content in the three samples after different pre-storage was almost the same and very low (moisture content max. 0.01%; see Table 4).

For Eskal 0.5–1.0 (Figure 14), there also is a comparable value for the angle of repose per test method for the three types of preconditioning. Even if the resulting moisture content in the bulk material after pre-storage at 90% r.h., at 0.04%, is about twice as high as that after pre-storage at 10% r.h. (Table 4), this increase of moisture content in this comparatively coarse-grained substance does not affect the flowability. For all three types of preconditioning, there is a similar tendency for this substance that the funnel test systematically results in too small angles of repose in comparison with the other methods. This can be explained by the fact that the coarse grains slide off the comparatively small platform and the cone of bulk solids cannot build up properly.¹

Eskal 10 is also calcium carbonate but in a fine powder form. Here, compared with Eskal 0.5–1.0, a different behaviour can be observed after different climatic preconditioning (Figure 15). For pre-storage at 10% r.h., it was not possible to measure the angle of repose for the two plate methods because the funnel outlet was blocked.

For each of the four test methods, the following tendencies are visible for Eskal 10: Compared with preconditioning at 10% r.h. (moisture content 0.05%; see Table 4), Eskal 10 has poorer flowability (higher angle of repose) after pre-storage at 50% r.h. (moisture content 0.15%). With preconditioning at 90% r.h. (moisture content 0.21%), the flowability of Eskal 10 is best (lowest angle of repose) for all four methods.

As can be seen from Table 4, a different climatic preconditioning has a statistically significant effect on the moisture content within the bulk material for this fine-grained substance. However, a general trend between the moisture content and the result of the angle of repose measurement cannot be derived from Figure 15. Kalman¹⁰ (see Section 2.1) examined a larger range of moisture contents, since the bulk material samples investigated were also sprayed with water

TABLE 6 Measurement results for the angle of repose of the three non-hazardous bulk solids for the dry climate (23°C, 10% r.h.)

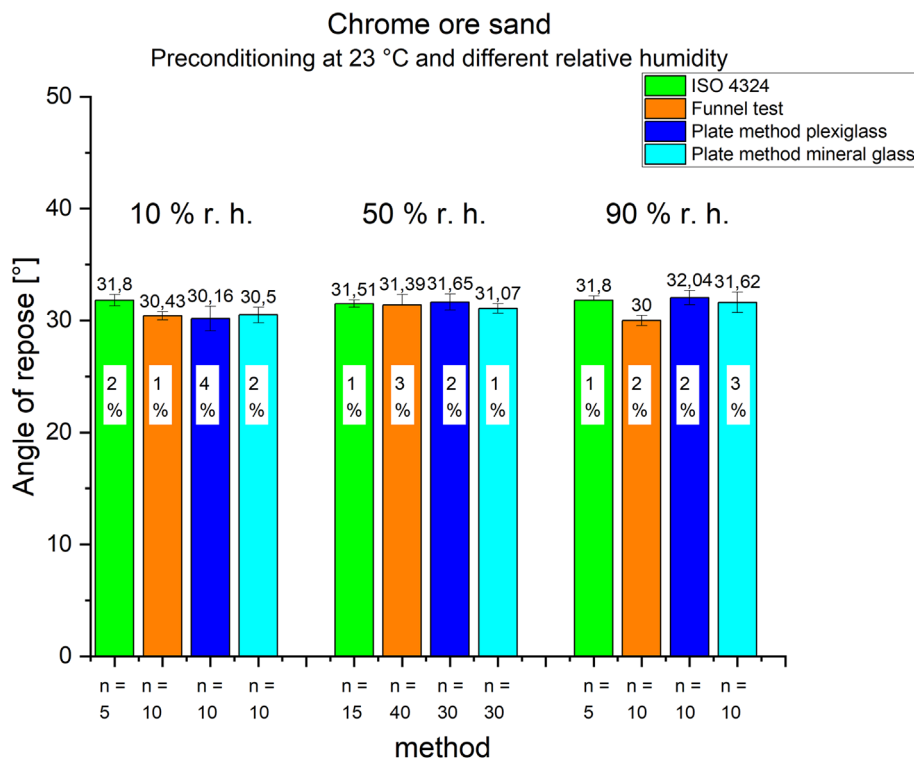
Substance name	ISO 4324			Funnel test			Plate method plexiglass			Plate method mineral glass		
	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [%]	$\bar{\alpha}$ [°]	σ [°]	c_v [%]	$\bar{\alpha}$ [°]	σ [°]	c_v [%]
Chrome ore sand	31.80	0.51	0.02	30.43	0.37	0.01	30.16	1.10	0.04	30.50	0.69	0.02
Eskal 10	31.80	0.51	0.02	37.60	5.94	0.16	Not applicable			Not applicable		
Eskal 0.5–1.0	35.68	0.49	0.01	31.50	1.56	0.05	35.72	1.15	0.03	33.99	1.73	0.05

TABLE 7 Measurement results for the angle of repose of the three non-hazardous bulk solids for the standard climate (23°C, 50% r.h.).¹

Substance name	ISO 4324			Funnel test			Plate method plexiglass			Plate method mineral glass		
	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [%]	$\bar{\alpha}$ [°]	σ [°]	c_v [%]	$\bar{\alpha}$ [°]	σ [°]	c_v [%]
Chrome ore sand	31.51	0.33	0.01	31.39	0.93	0.03	31.65	0.72	0.02	31.07	0.42	0.01
Eskal 10	33.96	1.34	0.04	45.28	4.14	0.09	17.71	4.40	0.25	23.68	6.29	0.27
Eskal 0.5–1.0	36.20	0.41	0.01	32.20	1.15	0.04	37.21	0.76	0.02	36.93	1.61	0.04

TABLE 8 Measurement results for the angle of repose of the three non-hazardous bulk solids for the humid climate (23°C, 90% r.h.)

Substance name	ISO 4324			Funnel test			Plate method plexiglass			Plate method mineral glass		
	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [–]
Chrome ore sand	31.80	0.41	0.01	30.0	0.45	0.02	32.04	0.64	0.02	31.62	0.91	0.03
Eskal 10	36.05	0.41	0.01	32.37	0.76	0.02	35.89	1.08	0.03	35.96	1.10	0.03
Eskal 0.5–1.0	30.87	0.81	0.03	36.21	4.47	0.12	16.59	3.36	0.26	11.87	1.37	0.12

**FIGURE 13** Angle of repose for chrome ore sand (different climates for preconditioning).

up to saturation to achieve high moisture contents. But this scenario of the preconditioning of bulk solids is unrealistic for the filling goods of dangerous goods packagings, whether they are non-hazardous

substitute filling substances or dangerous original filling goods. Within the scope of the current measurements, it was only intended to examine how different moisture contents, which are caused by a variation

FIGURE 14 Angle of repose for Eskal 0.5–1.0 (different climates for preconditioning).

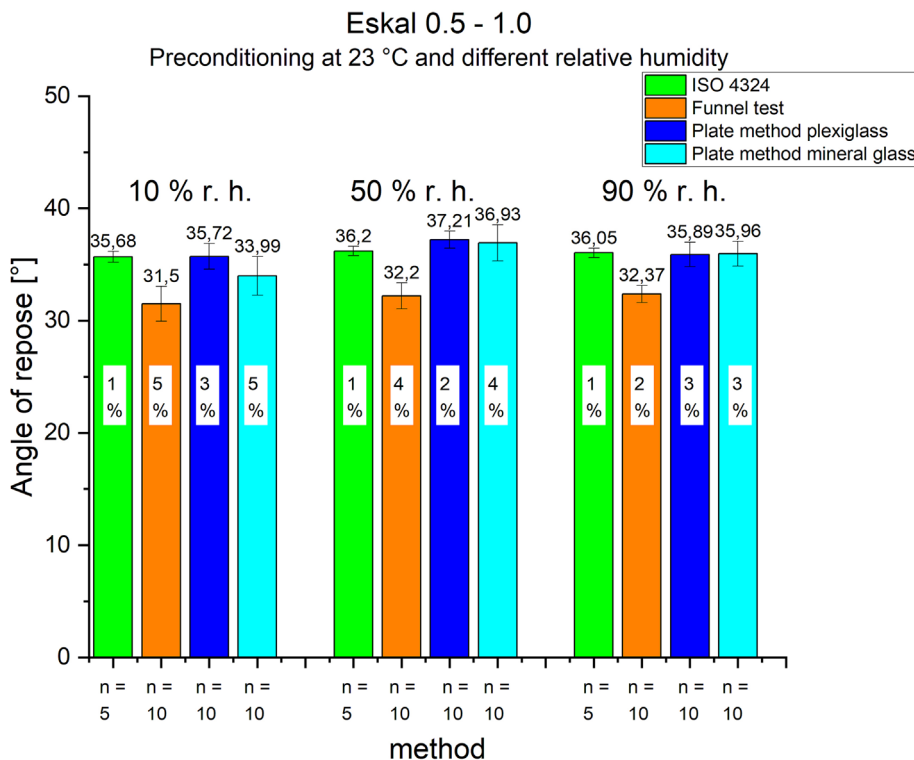
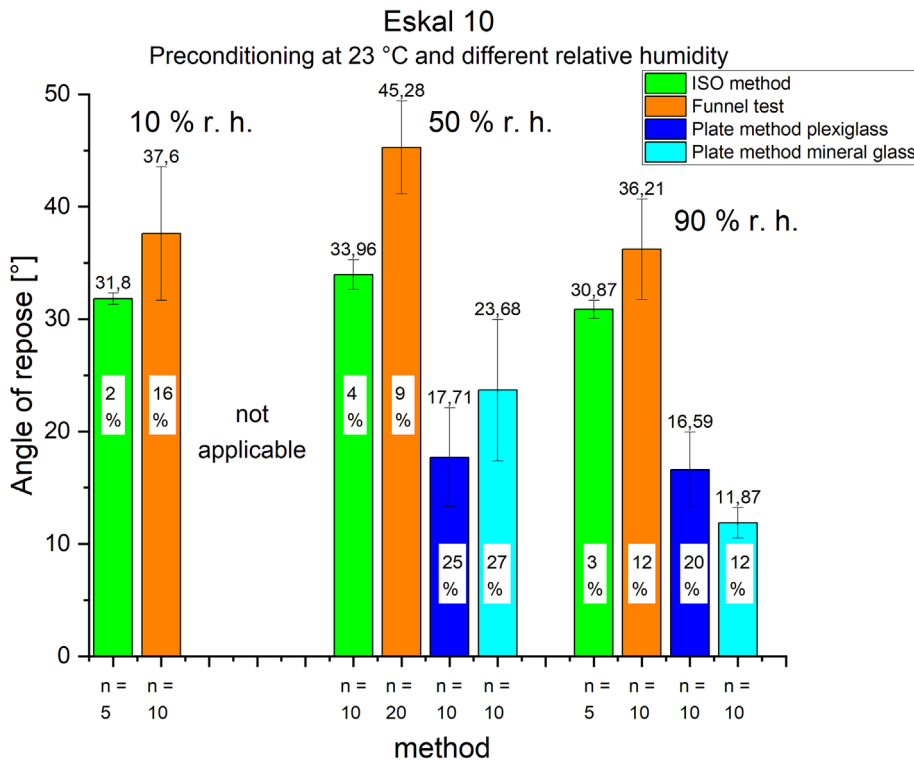


FIGURE 15 Angle of repose for Eskal 10 (different climates for preconditioning).



in the relative air humidity during the pre-storage of the bulk solids, affect the basic applicability and the results of the measurements for the angle of repose. As a result, compared with Kalman,¹⁰ there are smaller values for the moisture content, and the three measuring points for the moisture content are not sufficient to determine a

fundamental dependence of the angle of repose on the moisture content.

However, it is evident that for the fine-powdered Eskal 10, a different climatic pre-storage and a resulting different bulk material moisture have a significant influence on the basic applicability and

also on the overall results of the angle of repose measurements. Of the three substances examined, the fine-grained Eskal 10 is the most moisture sensitive. In a direct comparison between the two Eskal fractions, which have the same chemical composition, the coarse Eskal 0.5–1.0 is less sensitive to moisture. The influence of a different moisture content on the angle of repose is higher for finer bulk solids than for coarser bulk solids.²⁸

Of all four measurement methods, the ISO method is the most insensitive to fluctuations in moisture content of Eskal 10. One of the advantages of the ISO method is that the apparatus has a built-in stirrer and therefore the funnel cannot become clogged.

5.2 | Angle of repose—Hazardous substances (standard climate for preconditioning)

The mean angle of repose $\bar{\alpha}$, the standard deviation σ and the coefficient of variation c_v per substance and method are listed in Table 9

(standard climate). Figures 16–20 display the results for Sodium nitrate, ammonium bicarbonate, Biathlon 4D, Cantus and Pergafast.

For each substance, a statistical analysis of the angle of repose was performed by analysis of variance (one-way ANOVA and Kruskal–Wallis test) to evaluate the effect of the measurement methods. The measurement method forms the influencing variable (factor), and each measurement method is considered as group. The angle of repose is the dependent variable. The selected null hypothesis H_0 states that there is no difference between the mean values of the individual groups. The alternative hypothesis H_A is that at least two groups have significant differences in their expected values. The significance level is set at 0.05. The null hypothesis was rejected for all substances. This means that for all hazardous substances examined, the test method has a global statistically significant influence on the result of the angle of repose measurement. The pairwise comparison between the two plate methods showed that for all bulk materials, the results do not show any statistically significant difference.

TABLE 9 Measurement results for the angle of repose of the five hazardous bulk solids for the standard climate (23°C, 50% r.h.)

Substance name	ISO 4324			Funnel test			Plate method plexiglass			Plate method mineral glass		
	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [–]	$\bar{\alpha}$ [°]	σ [°]	c_v [–]
Sodium nitrate	34.99	0.61	0.02	33.66	1.64	0.05	31.92	1.68	0.05	30.97	1.63	0.05
Ammonium bicarbonate	35.22	0.64	0.02	20.62	2.27	0.11	30.98	1.71	0.06	30.81	2.12	0.07
Biathlon 4D	36.28	0.42	0.01	20.63	5.11	0.25	33.42	2.09	0.06	33.87	2.14	0.06
Cantus	28.97	1.41	0.05	22.42	4.33	0.19	29.16	2.49	0.09	30.26	1.38	0.05
Pergafast	51.38	0.58	0.01									

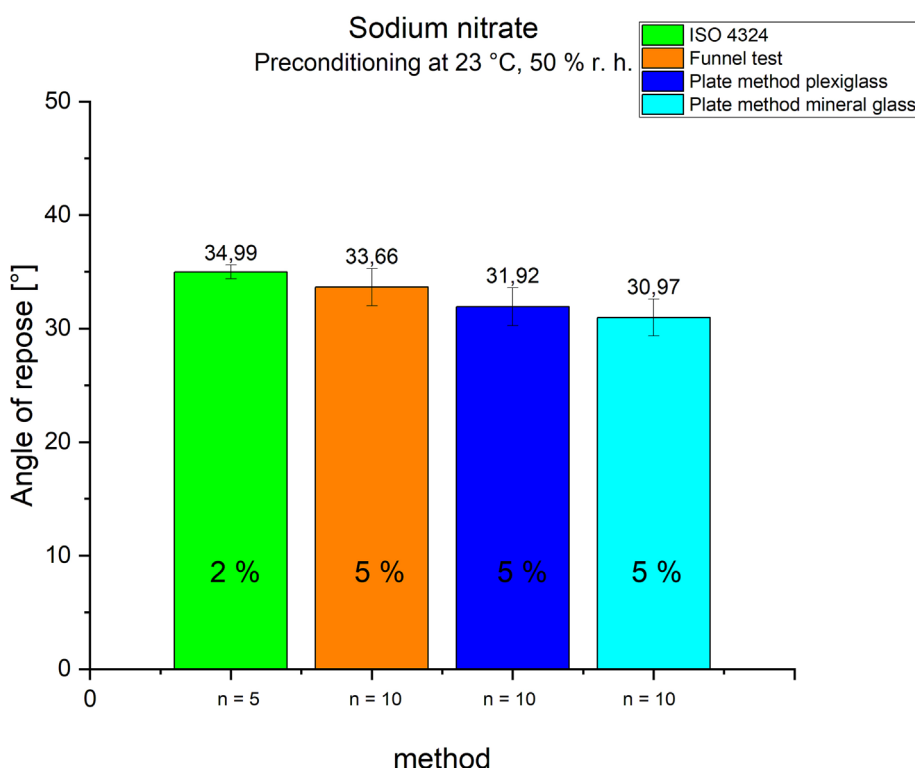


FIGURE 16 Angle of repose for sodium nitrate (standard climate for preconditioning).

FIGURE 17 Angle of repose for ammonium bicarbonate (standard climate for preconditioning).

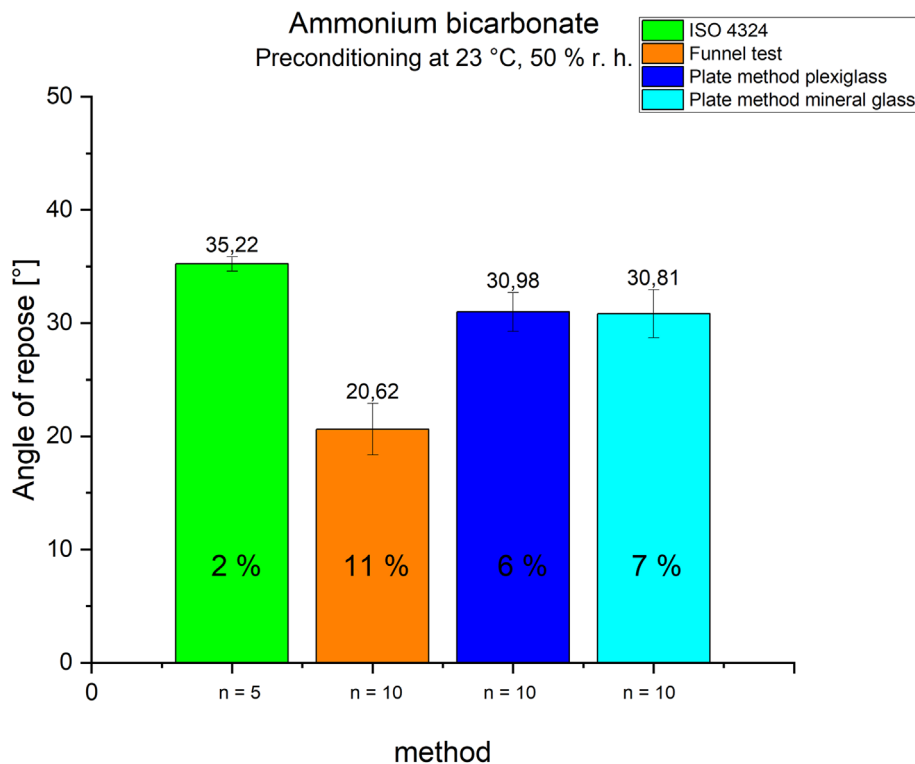
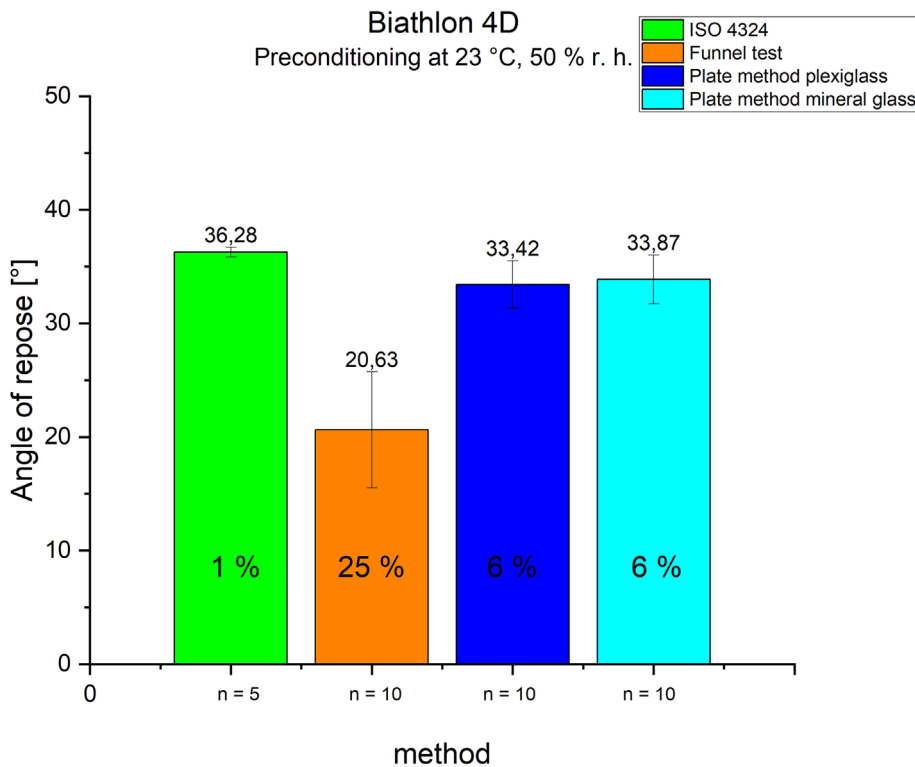


FIGURE 18 Angle of repose for Biathlon 4D (standard climate for preconditioning).



Therefore, for the substances examined, the plate material has no influence on the result of the angle of repose measurement.

A comparison of the different test methods for each substance is only possible to a limited extent, since the geometry of the respective apparatus, the material, the sample quantity used and the principle of

heap formation are different (see Section 4.2). The results of the different methods are therefore difficult to compare.^{12,16} In the following, the results and observations are discussed for each substance.

Although there is a significant difference in the angle of repose measurements for sodium nitrate (Figure 16) depending on the

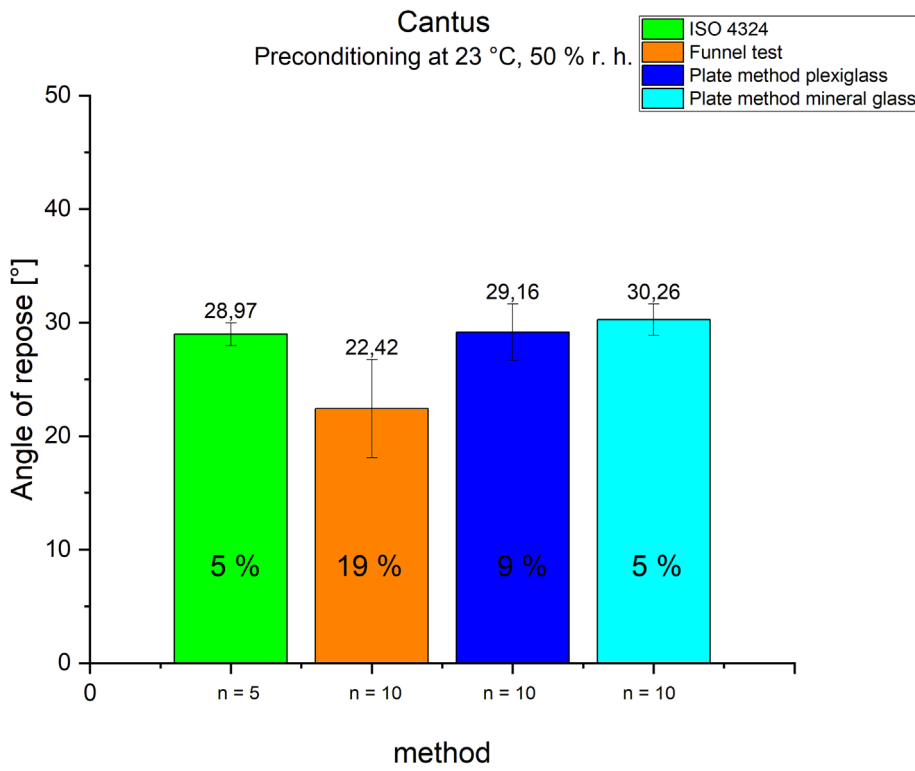


FIGURE 19 Angle of repose for Cantus (standard climate for preconditioning).

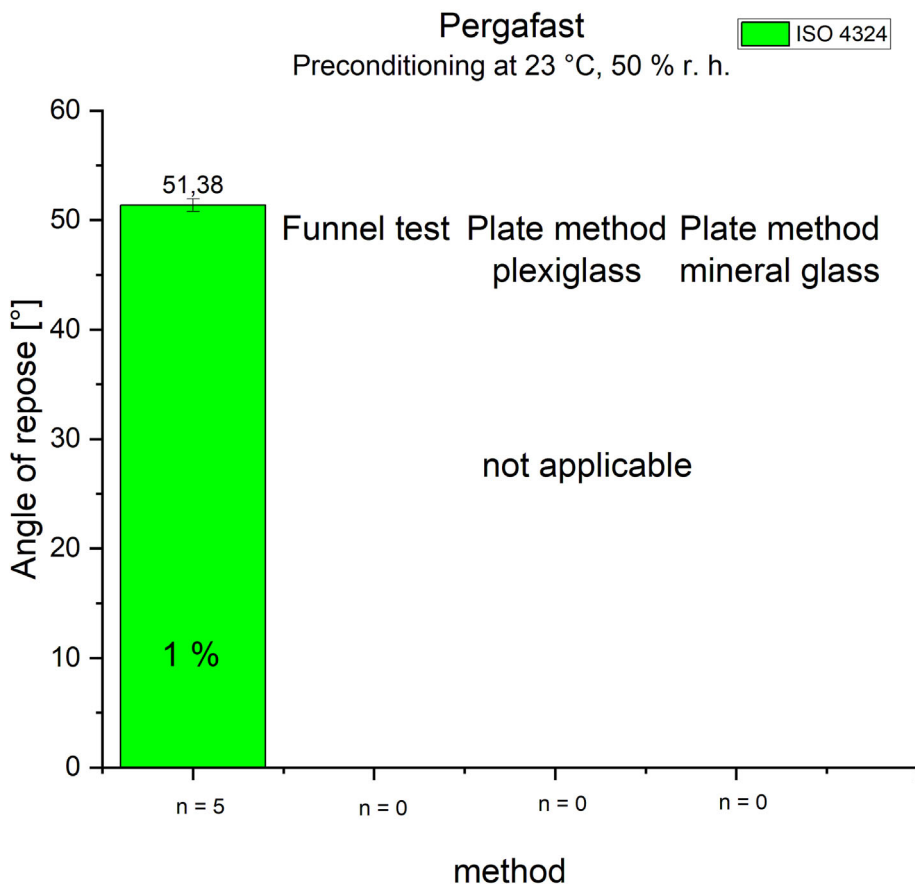


FIGURE 20 Angle of repose for Pergafast (standard climate for preconditioning).

method, all four methods provide a mean angle of repose in the range of approximately 31 to 35°, which is considered good flow behaviour according to Carr's classification (see Table 1). In all apparatus, sodium nitrate forms cones with almost straight slopes (see Figure 12 for plate method [plexiglass]), which makes it easier to measure the angle using the inclinometer (funnel test and plate methods). The coefficients of variation c_v is lowest for the ISO method (2%).

For ammonium bicarbonate (Figure 17), too, the application of the ISO method leads to the result with the smallest scatter ($c_v = 2\%$). However, the classification of the mean angle of repose according to Carr leads to a different assessment: The mean angle of repose of the ISO method ($\bar{\alpha} \approx 35^\circ$) is between good and medium flow behavior. The mean angle of repose of the two plate methods ($\bar{\alpha} \approx 31^\circ$) can be assigned to the transition between excellent and good flow behaviour. The mean angle of repose of about 21° determined with the funnel test is so small that it is not even listed in the classification according to Carr (Table 1). When comparing the cone shapes, the ISO method and the plate methods show an almost straight slope shape, but the funnel test has a convex cone shape (see Figure 21). This is an indication that with this individual configuration of bulk material and apparatus, the wall friction in relation to the surface of the base plate is high compared with the internal friction. As a result, the heap cannot build up properly and is flatter than with the other methods, and the angle of repose is lower. Since it is more difficult to apply the inclinometer to slope that is not straight, the resulting scatter is also highest here ($c_v = 11\%$).

Biathlon 4D, comparing the mean values of the four methods, shows the same trend as for ammonium bicarbonate, and the slope shapes are also comparable to ammonium bicarbonate: ISO method (see Figure 10) and plate methods: almost straight slope shape; funnel test: convex cone shape. The difference between the coefficients of

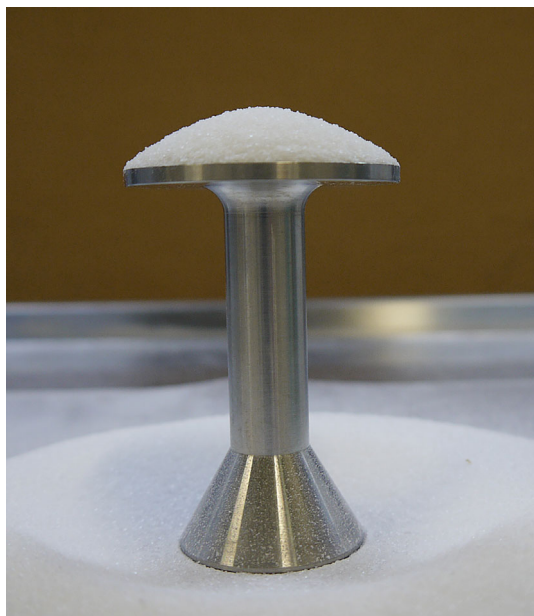


FIGURE 21 'Funnel test'—Ammonium bicarbonate—convex cone shape.

variation is greatest for this substance (ISO method: $c_v = 2\%$, funnel test: $c_v = 25\%$). The mean value for the angle of repose for the ISO test ($\bar{\alpha} \approx 36^\circ$) can be assigned to the area of fair flow behavior, for the two plate methods ($\bar{\alpha} \approx 33^\circ$) results a good flow behavior.

For Cantus (Figure 19), there are different cone shapes for the individual methods: a slightly convex cone shape for the ISO method, a concave cone shape for the funnel test (Figure 11) and straight slopes for the two plate methods. As a result, the heaps cannot build up properly with the ISO method and the funnel test and the cones are flatter than with the two plate methods. Although Cantus does not have an optimally straight flank shape with the ISO method, the scattering is again the lowest when using this method ($c_v = 5\%$, also with the mineral glass plate method). A classification of the mean angle of repose in the scheme according to Carr leads to excellent flow behaviour for all four methods. A pairwise comparison shows that there is no statistically significant difference between the mean angle of repose of the ISO method and that of the two plate methods. Even if the heap shape of this substance is slightly convex and therefore not optimal with the ISO method, the ISO method seems to be able to compensate for this.

Figure 22 shows the plate method (plexiglass) after Cantus has been tested. The plate method should not be used to test bulk solids with hazardous properties for two reasons. First, it is very time-consuming to clean this large and heavy apparatus. Since Cantus (like Biathlon 4D and Pergafast) is not water-soluble, the respective equipment and accessories such as funnels and measuring cups can only be cleaned with a solvent, in this case ethanol. However, cleaning such a large piece of equipment using flammable solvents also requires increased occupational safety measures.

Second, for reasons of occupational health and safety, it is not justifiable to use a sample quantity of 1.5 L of dangerous goods to carry out a single measurement, as it is prescribed for the plate method. Although the measurements were carried out under a large, walk-in fume hood, the process of flowing out of a funnel and forming a powder heap inevitably leads to dust deposits in the work area, especially in the case of fine, powdery substances. For substances with hazardous properties, this should be avoided. For these reasons, the use of the plate method for dangerous goods cannot be



FIGURE 22 'Plate method' (plexiglass)—Apparatus with dust deposits after testing cantus.

recommended. For the ISO method and the funnel test, on the other hand, only a smaller sample quantity of dangerous goods is required for each measurement (150 mL, 100 mL), and the subsequent cleaning of these smaller devices is also easier.

Only the ISO method was applicable for Pergafast (Figure 20) because the funnels of the funnel test and the plate methods became clogged (see Figure 23 for the funnel test). In the ISO apparatus, clogging of the funnel can be prevented by using the stirrer (Figure 24). The visible peaked tip of the powder cone often occurs with cohesive powders.²⁹ The mean angle of repose ($\bar{\alpha} \approx 52^\circ$) determined using the ISO method can be assigned to poor flow behavior. The coefficient of variation in this method is again small ($c_v = 1\%$).

As described in Section 2.1, the resulting heap shape is an indication of how the relation of the frictional forces within the bulk material turns out compared to the surface friction with respect to the base plate. This is therefore an individual correlation for the respective constellation of filling material and test apparatus. A comparison of the results shows that the funnel test in particular favours the formation of a flat, convex heap shape (ammonium bicarbonate and biathlon 4D), while the other test methods formed heaps with straight flanks. Schlick-Hasper et al.¹ already observed this tendency of a too-flat material cone in the funnel for the substances Eskal 150, Eskal 0.5–1.0, Escor 1.8–3.4 and Eskal 2.8–4.0, which always have coarser grains in this order. The reason given there was that comparatively coarse grains slip off the side of the relatively small stamp in the funnel test and the cone of bulk solids can therefore not build up properly. This is true in the case of coarser grains, but the relationship between the frictional

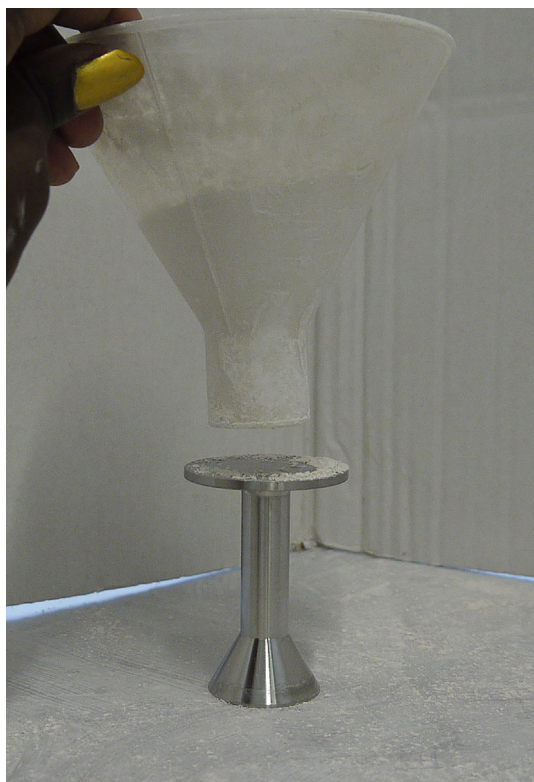


FIGURE 23 'Funnel test'—Pergafast—clogged funnel.

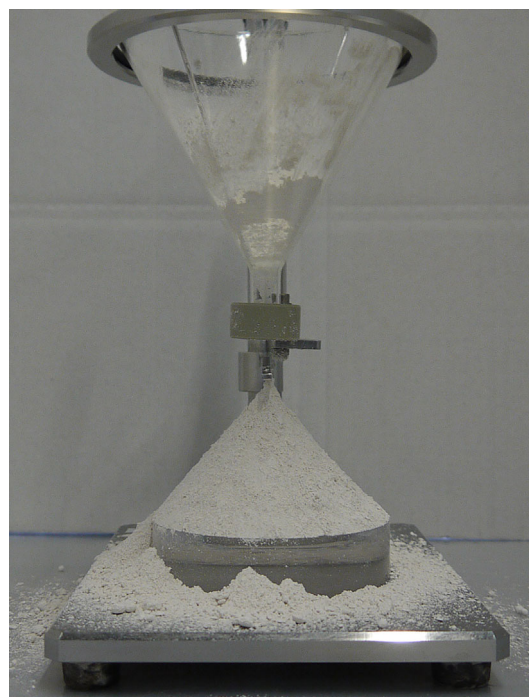


FIGURE 24 ISO method—Pergafast—peaked tip of powder cone.

forces can also be used to explain this phenomenon: With finer powders, the bulk material exhibits higher internal friction between the individual particles. The coarser the bulk material becomes, the more the internal friction within the bulk material loses importance compared with the surface friction, which favours the formation of a convex heap shape that leads to an angle of repose that is too small.

As already described,¹ measuring an angle of repose that is too small and specifying such a value as the minimum angle of repose in the certificate of approval could cause a loss of safety when transporting dangerous goods. In practice, this could lead to a substance with flow properties that are too good being filled into the type of packaging in question, which could result in a reduction in mechanical safety and an insufficient sift-proofness. For reasons of safety, the ISO method should therefore be preferred, since it provides the largest average angle of repose for almost all substances examined.

5.2.1 | Summary (angle of repose)

The results and observations using the four methods can be summarized as follows:

- Practical applicability: The ISO method is the only method that can be applied for all five hazardous substances, including Pergafast, that flows poorly according to Carr's scheme. For three out of four substances, the application of the funnel test leads to heaps that deviate from the ideal case of a straight flank or a conical shape and instead have a convex or concave cross-section. In such cases, the resulting heap is too flat in comparison and the angle of repose is therefore significantly lower than that of the other methods.

- **Repeatability:** Overall, the ISO method has the lowest scatter of the measured values for all substances, i.e. the best repeatability ($c_{v,max} = 5\%$). The other methods are more sensitive to operator influence, since the angle of repose is measured manually by applying an inclinometer. Especially in the case of heaps that do not have straight slopes, it can be difficult to apply the inclinometer in a reproducible manner.
- **Occupational health and safety:** All methods of measuring the angle of repose used in the German test labs for dangerous goods packagings are based on the principle that a defined quantity of powdery or granular substance is poured out so that a heap forms on an open surface or in an apparatus.¹ Regarding occupational safety, this procedure is considered critical when testing dangerous original filling goods with the plate method, in which 1.5 L filling goods are required for each individual measurement. Particularly in the case of very dusty filling substances, large amounts of dust are released and contaminate the laboratory environment, even if the test is carried out under a fume hood.¹ With the ISO method and the funnel test, this procedure is just about justifiable for occupational safety reasons, since the sample quantities used are smaller. But not only the release of dust is a problem, also the subsequent cleaning of the test equipment. With the plate method, this is particularly complex due to the large testing apparatus.
- **Safety when transporting dangerous goods:** Of the methods examined, the ISO method is to be given preference because it gives the largest mean value for the angle of repose and thus provides a conservative estimate with regard to safety when transporting dangerous goods.

Due to these four aspects, only the ISO method can be regarded as suitable for measuring the angle of repose of products with hazardous properties. Nevertheless, the Hausner ratio was also determined in this work as an alternative parameter for describing the flow behaviour of bulk solids, and a comparison was drawn with the angle of repose measurement; see next section.

5.3 | Hausner ratio—Hazardous substances (standard climate for preconditioning)

Table 10 shows the results for the determination of the Hausner ratio (mean value \bar{H} , standard deviation σ and coefficient of variation c_v) and the classification of the flow behaviour of the respective substance according to Carr¹⁴ (see Table 2). Figure 25 presents the

TABLE 10 Results for the Hausner ratio and aerated bulk density of the five hazardous bulk solids for the standard climate (23°C, 50% r.h.)

Substance name	ρ_a [kg/L]	\bar{H} [–]	σ [–]	c_v [–]	Classification (Table 2) ¹⁴
Sodium nitrate	1.40	1.09	0.01	0.01	excellent
Ammonium bicarbonate	0.89	Not applicable			-
Biathlon 4D	0.65	1.15	0.01	0.01	good
Cantus	0.70	1.10	0.01	0.01	excellent
Pergafast	0.49	1.39	0.02	0.01	poor

results. The measured values for the mean aerated bulk densities ρ_a are also given in Table 10.

It was not possible to determine the tapped density of ammonium bicarbonate, despite the slightly hygroscopic substance having been sieved beforehand. After the sieved substance was poured into the comparatively narrow measuring cylinder of the tapped volumeter, the surface was again so uneven due to agglomeration formation that no volume value could be read off. Therefore, no Hausner ratio could be determined for this bulk material.

The results of the Hausner ratio show a low scatter for the 5 substances examined (c_v max. 1%). The smallest Hausner ratio was determined for Sodium nitrate ($\bar{H} = 1.09$), which means excellent flow behaviour; the highest Hausner ratio was determined for Pergafast ($\bar{H} = 1.39$), which indicates poor flow behaviour.

A comparison of the flowability assessment obtained by determining the Hausner factor and by measuring the angle of repose using the ISO method shows the following: For two of the examined substances, the flowability classification based on the ISO method results in a slightly poorer flow behaviour (sodium nitrate: 'good', Biathlon 4D: 'fair'). Therefore, the assessment using the ISO method leads to safety-related conservative results for two of the substances examined. For Cantus and Pergafast, the rating is the same ('excellent' or 'poor'). This means that the assessment of the flow behaviour leads to similar results for both methods. However, a general statement would only be possible on the basis of a larger number of substances examined.

5.3.1 | Summary (Hausner ratio)

The results and observations of determining the Hausner ratio can be summarized as follows:

- **Practical applicability:** The underlying measurements for tapped density and aerated bulk density were only applicable for four of the five hazardous substances. Due to the formation of agglomerates within the measuring cylinder with the hygroscopic ammonium bicarbonate, the tapped density measurement could not be carried out. Therefore, the Hausner ratio could not be determined for all substances examined.
- **Repeatability:** The maximum coefficient of variation resulting from the application of this procedure to the five substances is 1%. The repeatability is thus better than the ISO method for angle of repose measurement.

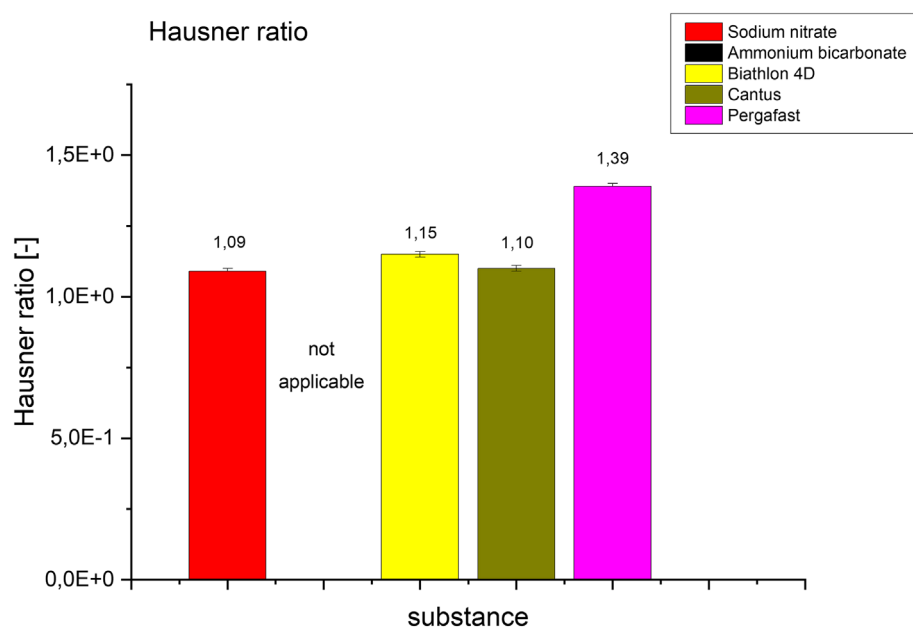


FIGURE 25 Hausner ratio for the five hazardous substances (standard climate for preconditioning).

- Occupational health and safety: For measuring aerated bulk density and tapped density, it is also necessary to decant the respective substance. However, the sample quantity is taken up in a measuring cylinder with a defined volume and a significantly smaller sample amount is spilled freely onto a surface. This leads to easier handling and cleaning of the equipment compared to the measurement of the angle of repose.¹ With regard to occupational health and safety, this approach can be rated as more favourable, at least in relation to the plate method.
- Safety when transporting dangerous goods: The assessment of whether the determination of the Hausner ratio in the assessment of the flow properties is equivalent to the result of the angle of repose measurement does not lead to a clear result. This would require a larger database to find out which approach leads to safety-related conservative results for certain types of filling goods.

6 | CONCLUSION

The flow properties of powdered or granular substances affect safety when transporting dangerous goods. The test practice in the test centres for dangerous goods packagings in Germany requires a simple, reliable method that can also be used safely for dangerous original contents.

In Part 1 of the investigations,¹ it was generally assessed as critical to carry out angle of repose measurements on dangerous goods at all. Therefore, it was suggested to use the Hausner ratio to assess the flow behaviour of hazardous powdery or granular substances instead. This statement was based on measurements that had been carried out exclusively on non-hazardous goods.

However, the concrete series of measurements on exemplary substances with hazardous properties that has now been carried out showed that the application of the ISO method for measuring the

angle of repose can also be used and justified in principle from the point of view of occupational health and safety. This method has the best repeatability of angle of repose measurement methods currently applied in the testing laboratories. Also, the ISO method is the only method that could be applied to all substances examined. When determining the Hausner ratio, on the other hand, problems can arise when performing the tapped density measurement for substances that tend to agglomerate.

With regard to safety when transporting dangerous goods, a conservative assessment of the flow properties is necessary. The application of the funnel test for measuring the angle of repose systematically yields too small results for bulk materials whose internal friction is small compared to the wall friction in this apparatus and which therefore form convex material cones.

This can lead to an impairment of safety when transporting dangerous goods if, based on such a measurement, the minimum angle of repose in the certificate of approval is specified as too low and the user therefore fills the packaging with a product having too good flowability. The ISO method is less sensitive to deviations from the ideal cone shape with straight flanks. The angle of repose measured with the ISO method is therefore larger compared to the funnel test and represents a higher level of safety when stated as the minimum angle of repose.

In summary, both the determination of the angle of repose with the ISO method and the determination of the Hausner ratio are generally suitable for use in the test centres for dangerous goods packagings. The principle of a safety-related conservative approach should also be considered if a minimum Hausner ratio is to be specified in the certificate of approval instead of a minimum angle of repose. However, further investigations are needed to compare the flowability assessment based on the ISO method and the determination of the Hausner ratio.

The relative humidity during preconditioning can have a significant influence on the moisture content of finely powdered substances and thus the result of the angle of repose measurement.

The results show that for a valid performance of measurements to determine the flow properties, not only a suitable test method has to be selected, but also a controlled preconditioning of the bulk solids has to take place. Therefore, for reasons of reproducibility, type and duration of the climatic preconditioning of the filling substances should always be specified by the test centres for dangerous goods packagings in their test report.

However, in order to determine the exact functional relationship between the moisture content and the result of the angle of repose measurement, further measurements with more measuring points and bulk materials are required.

Future investigations could also aim to develop a test method for sift-proofness for bags and FIBC based on the knowledge gained so far and thus to further improve safety when transporting dangerous goods.

TABLE OF SYMBOLS

Symbol	Description	Unit
c_v	Coefficient of variation	-
H	Hausner ratio	-
h	Height of the pile	m
m_d	Dry solids mass	kg
m_w	Water mass	kg
X	Moisture content	-
x	Particle size	μm
$x_{max,3}$	Largest particle size (based on quantity type volume)	μm
$x_{min,3}$	Smallest particle size (based on quantity type volume)	μm
$x_{mod,3}$	Mode (based on quantity type volume)	μm
$x_{10,3}$	Particle size below which 10% of the particle quantity is located (based on quantity type volume)	μm
$x_{50,3}$	Median (particle size below which 50% of the particle quantity is located; based on quantity type volume)	μm
$x_{90,3}$	Particle size below which 90% of the particle quantity is located (based on quantity type volume)	μm

TABLE OF GREEK SYMBOLS

Symbol	Description	Unit
α	Angle of repose	°
ρ_a, ρ_t	Aerated bulk density, tapped bulk density	kg/m^3
σ	Standard deviation	°

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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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