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TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 4-2: Nano-enabled electrical energy storage – Physical characterization of cathode nanomaterials, density measurement

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Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-4-2, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems.

The text of this Technical Specification is based on the following documents:

Enquiry draft	Report on voting
113/289/DTS	113/328/RVC

Full information on the voting for the approval of this Technical Specification can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- transformed into an International Standard,
- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

A bilingual version of this publication may be issued at a later date.

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INTRODUCTION

Compared with normal bulk materials, nanomaterials often exhibit many unique properties, such as mechanical, thermal, magnetic, optical and electrochemical properties. Decreasing particle size of the cathode materials, e.g. lithium iron phosphate (LFP), down to nanoscale greatly enhances their electrochemical performance. For example, smaller particle size will shorten the diffusion length of lithium ion during lithium intercalation/de-intercalation process. Higher surface area will increase the electrode/electrolyte contact area, and subsequently improve the high current charge/discharge rates. Furthermore, the particle surfaces may introduce a sub-gap, which can smooth the electrode discharge curve, then help to prolong the cycling life of the electrode.

Density is one of the key control characteristics for cathode nanomaterials and affects the performance of electronic energy storage devices significantly. At an appropriate density, the electrochemical performance, such as low-temperature and high-temperature charge/discharge, and the ratio of charge/discharge capability, will be dramatically increased.

Among different densities, changing the compacted density of cathode nanomaterials to a suitable value can increase their charge capacity, decrease the internal resistance, lower the polarization effect, increase cycling life of electrical energy storage devices, and improve the usability of electrical energy storage devices. It is important to find the optimum compacted density for the electronic energy storage device design. If the compacted density is too large or too small, the intercalation and de-intercalation of ions will be affected. In general, compacted density is in a positive correlation to the device's specific capacity, and is considered as one of the key parameters for material energy density.

Rolling density affects the electrochemical performance characteristics of cathode nanomaterials in a similar way. Rolling density indicates the ratio of the mass of coating slurry compound to its volume. Rolling density is a valuable quantity not only for evaluating the volumetric energy density, but also for selecting a cathode nanomaterial candidate for Hybrid-Electric Vehicles (also known as HEVs) and Electric Vehicles (also known as EVs).

Both of these two types of properties need to be considered in the density assessment of a nano-enabled electrical energy storage device. Comparable results will be used to judge the consistence of cathode nanomaterials, which relates to performance and safety issues. Therefore, a standardized density measurement procedure for cathode nanomaterials becomes indispensable to its users for comparing the values of nanomaterials from different suppliers.

This standardized method is intended for use in comparing the characteristics of cathode nanomaterials in the study stage, not for evaluating the electrode in end-products. The method is applicable to materials exhibiting function or performance only possible with nanotechnology, intentionally added to the active materials to measurably and significantly change the characteristics of electrical energy storage devices.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 4-2: Nano-enabled electrical energy storage – Physical characterization of cathode nanomaterials, density measurement

1 Scope

This part of IEC 62607, which is a Technical Specification, provides a standardized method for the determination of the density of cathode nanomaterials in powder form used for electrical energy storage devices. This method provides users with a key control characteristic to decide whether or not a cathode nanomaterial is usable, or suitable for their application.

This document includes

- definitions of terminology used in this document,
- recommendations for sample preparation,
- outlines of the experimental procedures used to measure cathode nanomaterial properties,
- methods of interpretation of results and discussion of data analysis,
- case studies, and
- references.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004-1, *Nanotechnologies – Vocabulary – Part 1: Core terms*

3 Terms, definitions, and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1.1
cathode nanomaterial
material used as a cathode in a nano-enabled energy storage device which contains a fraction of nanomaterial and exhibits function or performance made possible only with the application of nanotechnology

Note 1 to entry: The cathode is a multilayered foil consisting of (1) an aluminium current collector, (2) an optional adhesion promoting carbon layer (to enhance cathode layer adhesion if necessary) and (3) the cathode layer. This cathode layer consists of the active phase (e.g. lithium containing mixed oxides or phosphate, such as LFP), a conducting phase (carbon black) and an organic binder (PVDF).

3.1.2
compacted density
ratio of the mass of powder to the volume it occupies after it has been subjected to compression under a certain pressure

3.1.3
rolling density
ratio of the mass of the rolled active material to its volume after being coated on a substrate

3.1.4
die
tool designed for containing and forming the powdered samples during compression, which is made from hard materials (e.g. tungsten carbide)

Note 1 to entry: A die is usually in a cylinder shape and contains two punches for producing compacts, and is of the floating type or of the type suspended from a spring, in order to ensure dual action pressure.

3.1.5
press
mechanical device designed for generating and applying pressure upon the die to compress the sample, which is capable of applying sufficient force to the die surface with an accuracy of ±1 %

3.2 Abbreviated terms

LFP lithium iron phosphate, $LiFePO_4$

PVDF polyvinylidene fluoride

4 Sample preparation methods

4.1 Sieving

Sample should be homogeneous particulate powder with uniform sizes. If big chunks or large agglomerates exist, they should be removed by sieving (150 mesh) in order to avoid cracking, delamination and local ununiformity in the compacted density.

4.2 Drying

Dry the sample in an oven at a temperature above 100 °C until dry. For example, one drying protocol may consist of two hours in an oven at 105 °C. However, other samples may require longer time to be sufficiently dry for use in nano-enabled electrical energy storage devices.

5 Test methods

5.1 Compacted density

5.1.1 General

Weigh the desired mass of sample, place the sample in the die (The parameters and tolerances are indicated in Figure A.1 and engineering drawing is shown in Figure A.2 in Annex A.), and then put the die in the middle of the power compressor. Adjust the settings on the powder compressor until the desired pressure is reached. Maintain the pressure for a certain duration, then take out the cylindrical sample and measure its height. The compacted density is calculated by dividing the mass of cathode nanomaterials by the volume.

5.1.2 Apparatus

5.1.2.1 Analytical balance

The analytical balance used shall have a resolution of 0,01 g.

5.1.2.2 Powder compressor

The powder compressor consists of two parts:

a) a die, having the three-dimensional appearance shown in Figure A.1 and Figure A.2;

b) a die compressor, having the appearance shown in Figure 2.

5.1.2.3 Vernier caliper

The resolution of an appropriate vernier caliper used should be 0,02 mm.

5.1.3 Measurement steps

Measurement steps are as follows:

a) Turn on the electronic balance, weigh a certain mass of sample (suggested range: 1 g to 10 g and record the mass (m) in grams. Care should be taken to ensure that the change of m during sample transfer and density measurement is minimal.

b) Take out the die from the powder compressor and clean it with dustless paper, transfer the weighed sample into the die (if it cannot be filled all at once, do it as many times as necessary), make sure the powder is evenly distributed in the die, then cap the die (Figure 1).

c) Gently place the die in the middle of the compressor and fix the hand wheel clockwise. Increase the pressure to the desired setting (the value can vary depending on the type of powder, such as particle size, shape. For LFP, it is suggested to be 10 MPa to 20 MPa, which is defined by the integrity of the sample cylinder). Maintain the pressure for 1 min to 2 min, and then release the pressure slowly.

d) Take out the die (Figure 2) and then take out the sample – the sample should be a cylinder; measure the height (h) and diameter (d) using the vernier caliper and record h and d in millimetres.

In case of nanomaterials with which it is difficult to form intact cylinders, it is recommended to measure the sample height when it is still with the upper and lower pads, and then obtain the value by subtracting the predetermined pad heights.

5.1.4 Data analysis / interpretation of results

Compacted density is calculated by Formula (1):

$$\rho = \frac{m}{v} = \frac{4m}{\pi d^2 h \times 10^{-3}} \quad (1)$$

where

ρ is the compacted density, g/cm^3;

m is the mass of the powder, g;

v is the volume of powder after compression, cm^3;

π is the ratio of the circumference of a circle to the diameter;

d is the diameter of sample cylinder, mm;

h is the height of sample after compaction, mm.

Perform three individual measurements for the same sample, and then take the arithmetical average value if they pass the repeatability test, and report the final result, precise to 0,1 g/cm^3.

IEC

Figure 1 – Appearance of die for compacted density measurement

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Figure 2 – Appearance of die with compressor

5.1.5 Precision of the method

5.1.5.1 Repeatability

The results of three independent single test results, obtained using the same method on identical testing material in the same laboratory by the same operator using the same equipment within a short interval of time, should not differ by more than 2 % of the arithmetic average of the three results.

Reject the results if the difference exceeds the indicated repeatability value and carry out new determinations.

5.1.5.2 Reproducibility

The average results of the duplicate tests, obtained using the same method on identical materials in each of two laboratories' testing materials, are expected to agree within 5 %.

5.2 Rolling density

5.2.1 General

Bind the cathode active materials to form a paste with a suitable viscosity. Coat the paste on the substrate (aluminium) followed by drying until the solvent is completely evaporated. And then the electrode composite is pressed through the rolling machine. Punch the rolled electrode composite in a certain area (configuration as shown in Figure A.6, step B). Rolling

density will be obtained by calculating the mass of cathode materials over the volume after rolling.

5.2.2 Apparatus

5.2.2.1 Balance

The balance used in the experiment should be capable of weighing to within ±0,01 g.

5.2.2.2 Micrometer

The micrometer used in the experiment should be capable of measuring to within ±0,001 mm.

5.2.2.3 Coating machine

The coating machine is shown in Figure A.6, step A.

5.2.2.4 Rolling machine

The rolling machine is shown in Figure A.6, step B.

5.2.3 Measurement steps

Measurement steps are as follows:

a) Mix the cathode active material with a suitable amount of binder and conductive materials in water or NMP (1-Methyl-2-pyrrolidinone), etc. as the solvent, stir the mixture to form a suitable viscosity paste.

b) Inject the paste into the coating machine and uniformly coat the paste on the substrate (aluminium) and then dry. This procedure should be conducted below a certain humidity as humidity may influence the property of coating. For LFP to be mixed into NMP, the humidity should be controlled in the range 0 % to 50 %.

c) Rolling process: Place the cathode into the groove of the rolling machine to form the rolled cathode.

d) Measurement: Select the shape and size of the cathode electrode and substrate – area (symbol: s), mass (symbol: $m_{\text{Electrode}}$ and $m_{\text{Substrate}}$), thickness (symbol: $h_{\text{Electrode}}$ and $h_{\text{Substrate}}$), respectively.

5.2.4 Data analysis / interpretation of results

Rolling density is calculated by Formula (2):

$$\rho = \frac{m}{v} = \frac{m_{\text{Electrode}} - m_{\text{Substrate}}}{s\left(h_{\text{Electrode}} - h_{\text{Substrate}}\right) \times 10^{-3}} \tag{2}$$

where

ρ is the rolling density, g/cm^3;

m is the powder mass of cathode electrode, g;

v is the powder volume of cathode electrode after rolling, cm^3;

$m_{\text{Electrode}}$ is the mass of cathode electrode, g;

$m_{\text{Substrate}}$ is the mass of cathode substrate, g;

s is the area of cathode electrode after rolling, mm^2;

$h_{\text{Electrode}}$ is the thickness of cathode electrode after rolling, mm;

$h_{\text{Substrate}}$ is the thickness of cathode substrate, mm.

The final results shall be the arithmetic average value after three measurements, precise to 0,1 g/cm^3.

5.2.5 Repeatability of the method

The results of three independent single tests, obtained using the same method on identical testing material in the same laboratory by the same operator using the same equipment within a short interval of time, should not differ by more than 2 % of the arithmetic average of the three results.

Reject the results if the difference exceeds the indicated repeatability value and carry out new determinations.

6 Uncertainty

Currently, the uncertainties associated with measuring the compacted and rolling densities of cathode nanomaterials should be estimated from various origins as listed below:

a) uncertainties associated with weighing the mass of the powder, which include the balance calibration, weighing operation, and spills when transferring the sample;

b) uncertainties associated with measuring the volume of the compressed and rolled sample, which include caliper calibration, inhomogeneity in disc flatness, and baseline determination.

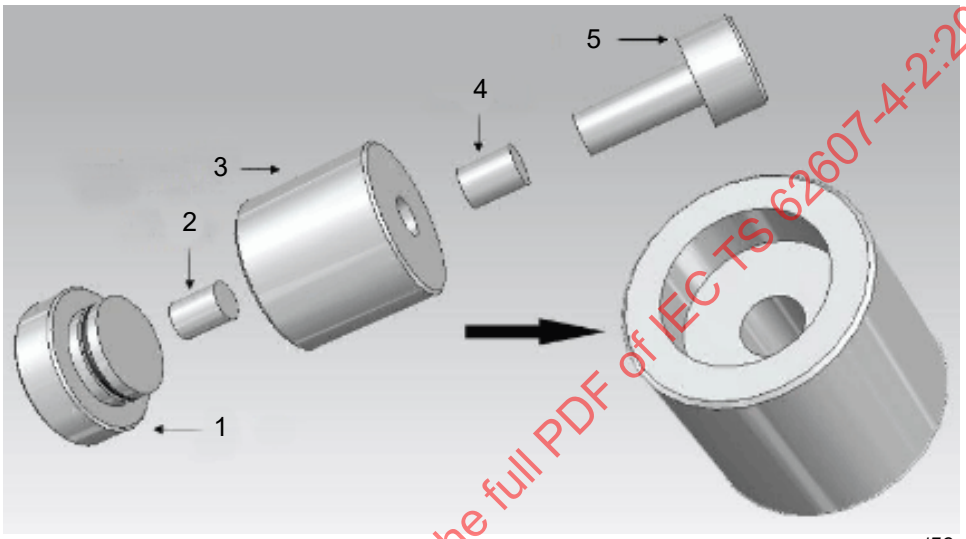
Annex A
(informative)

Case study

A.1 Sample preparation

A.1.1 Schematic figures of die for measuring compacted density and rolling density

Schematic figures of die and rolling machine are shown in Figures A.1 to A.3.



Key

1 die base
2 lower pad
3 sample container
4 upper pad
5 punch

Figure A.1 – Three-dimensional schematic of die for compacted density measurement

Dimensions in millimetres

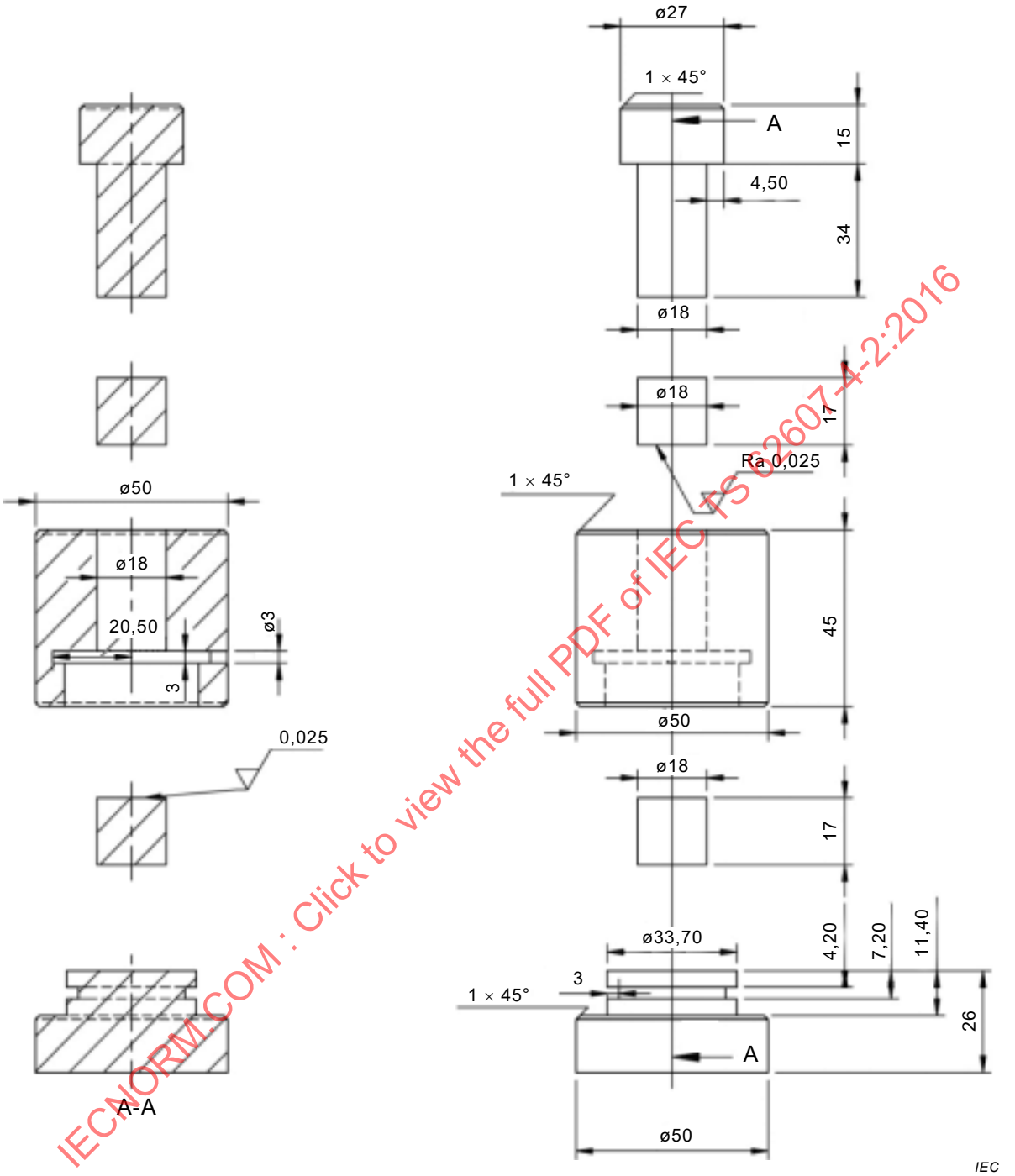
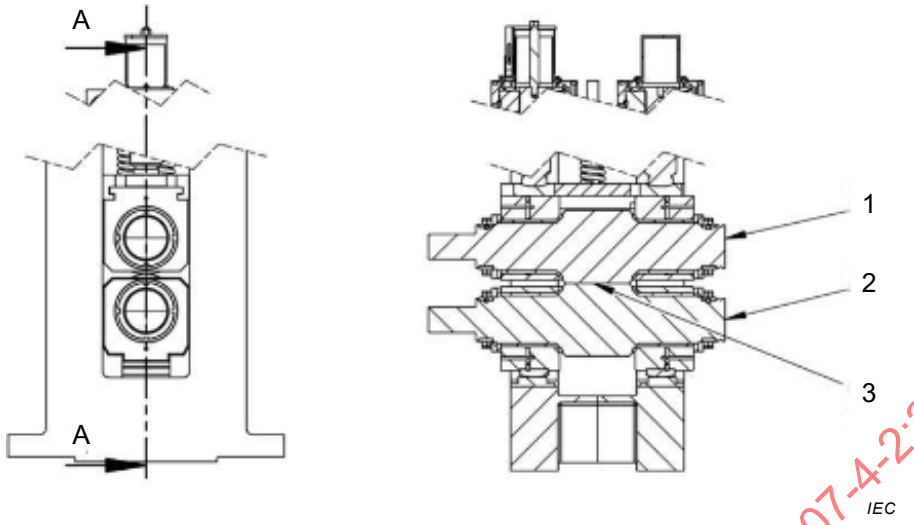


Figure A.2 – Engineering schematic of die for compacted density measurement



Key

1 upper roller

2 bottom roller

[a] Cathode sheet is condensed through the gap by rolling.

Figure A.3 – Schematic of rolling machine for rolling density measurement

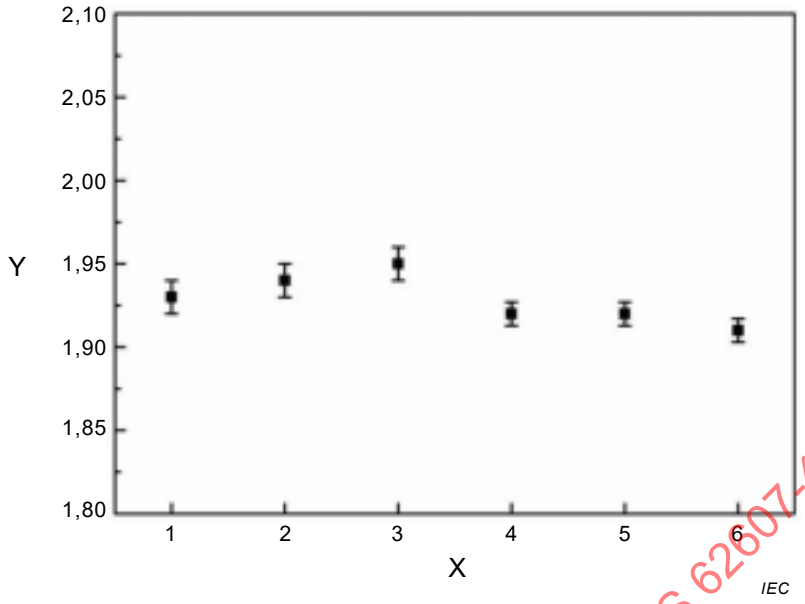
A.1.2 Compacted density measurement results for LFP nanomaterial

Measurement results for sample A are given in Table A.1 and represented graphically in Figure A.4.

Table A.1 – Measurement method consistency and measurement results of sample A

Sample	No.	Mass (g)	Compacted density (g/cm^3)	Average value (g/cm^3)	Absolute deviation (g/cm^3)	Relative deviation (%)	Standard deviation (g/cm^3)
Sample A	1	4,00	1,93	1,94	−0,01	0,52	0,010
	2	4,00	1,94		0	0	
	3	4,00	1,95		0,01	0,52	
Sample A	4	2,50	1,92	1,92	0	0	0,007
	5	2,50	1,92		0	0	
	6	2,50	1,91		−0,01	0,52	

Results from Table A.1 show that the deviation of compacted density in different measurements of sample A is lower than 2 % and 5 %.



X index of experiments

Y compacted density (g/cm^3)

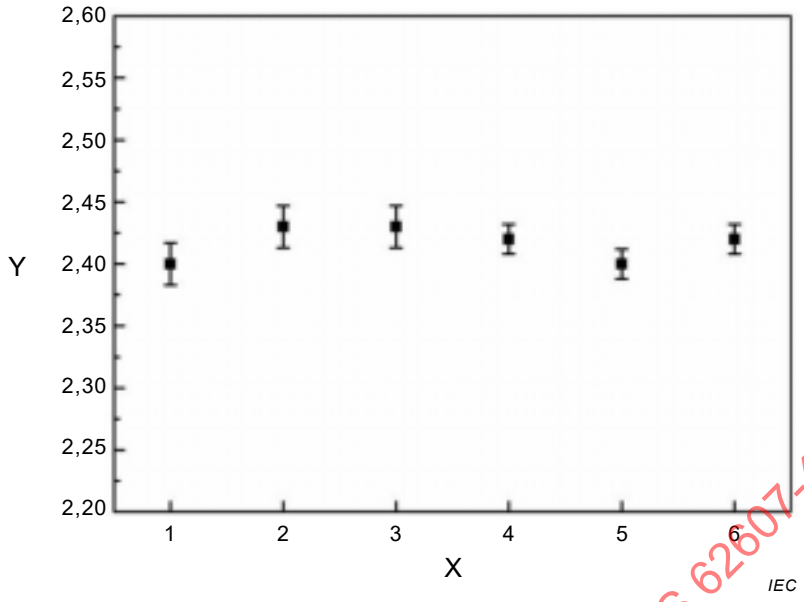
Figure A.4 – Results consistency of sample A in Table A.1

Measurement results for sample B are given in Table A.2 and represented graphically in Figure A.5.

Table A.2 – Measurement method consistency and measurement results of sample B

Sample	No.	Mass (g)	Compacted density (g/cm^3)	Average value (g/cm^3)	Absolute deviation (g/cm^3)	Relative deviation (%)	Standard deviation (g/cm^3)
Sample B	1	4,00	2,40	2,42	−0,02	0,83	0,017
	2	4,00	2,43		0,01	0,41	
	3	4,00	2,43		0,01	0,41	
Sample B	4	2,51	2,42	2,41	0,01	0,41	0,012
	5	2,51	2,40		−0,01	0,41	
	6	2,50	2,42		0,01	0,41	

Results from Table A.2 show that the deviation of compacted density in different measurements of sample B is lower than 2 % and 5 %.



X index of experiments

Y compacted density (g/cm^3)

Figure A.5 – Results consistency of sample B in Table A.2

A.2 Rolling density sample preparation case study

A.2.1 Procedures of rolling density sample preparation

Procedures of rolling density sample preparation are shown in Figure A.6.