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TECHNICAL SPECIFICATION

colour inside

Nanomanufacturing – Key control characteristics – Part 3-2: Luminescent nanoparticles – Determination of mass of quantum dot dispersion

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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 62607-3-2, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology standardization for electrical and electronic products and systems.

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

Enquiry draft	Report on voting
113/243/DTS	113/348/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 document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts of 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 document. At this date, the document 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- withdrawn,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

Quantum dots (QDs) are crystals of semiconductor materials measuring typically but not limited to 2 nm to 15 nm in a given dimension and could exhibit desirable absorption and emission properties. QDs can be synthesized by a variety of methods, the colloidal method being the most common. Through the colloidal method, QDs are synthesized in the presence of stabilizing ligands to maintain colloidal stability. These ligands can remain present after purification and are an important component of QD dispersibility and stability and can impact the optical properties. Often, QD samples are provided as a stable dispersion instead of a dried powder. The method specified in this document provides a means to determine the mass of QDs in that dispersion.

In addition to the semiconductor material and the tightly bound stabilizing ligands, QD dispersions could potentially contain unreacted precursors, side-products of the precursors, and free ligands. Due to the difficulty of removing and determining the amount of these impurities, the dried mass is not sufficient for measuring QD mass. Instead, a method is chosen that will remove or decompose the impurities while leaving the semiconductor material intact.

One method to volatilize or decompose the impurities and surfactant ligands is by heating the QD sample to high temperatures (650 °C). Heating QD samples to such high temperatures is typically destructive to the QD sample, so this analysis would need to be performed on a small portion that is representative of the entire sample.

Thermogravimetric analysis (TGA) is a convenient tool for accurately measuring mass loss of a small amount of sample (10 mg to 50 mg) when heated to high temperatures under either an N_2 or O_2 environment. The general procedure is to add an amount of dispersed material to the TGA pan, remove the dispersing solvent, and heat the pan to 650 °C in the TGA. The leftover mass is mostly the inorganic content of the QD material. Compared to other instrumentation such as inductively coupled plasma mass spectrometry, TGA is convenient, ubiquitous, and can give a direct measure of the inorganic mass of a quantum dot mixture.

The following are potential errors to the TGA-based method:

- Under an N_2 environment, it is possible that instead of volatilizing, the impurities will decompose and be converted into graphite or another non-volatile product. This will result in a measured mass that is greater than just the mass of the semiconductor material, whereas heating organic precursors to 650 °C typically results in only a minimal amount of residual mass (< 2 % of initial mass).
- Under an O_2 environment, heating samples can result in added mass from oxidation of metal and chalcogenide species. To avoid this complication, samples are heated under an N_2 environment.
- Inorganic-based impurities can leave a residual mass upon heating. These impurities (such as carboxylate salts, phosphonate salts) are typically not soluble in commonly used dispersing solvents (hexanes, toluene) and the concentration of these impurities in the dispersion is expected to be low, if a proper solvent is used, unless they are being solubilized by the QD material. If a solvent for potential impurities is used for the dispersion, then additional analysis may be necessary to determine the level of inorganic impurities. For safety purposes, this method should not be used for solutions containing perchlorate salts as this may cause an explosion.
- Tightly bound surface ligands may not fully decompose under these conditions. It is possible that the surface ligands would be converted into graphite instead of volatilizing. In this case, the residual ligand mass would be included in the mass calculation.
- Certain metal or main group elements may volatilize from the quantum dot depending on the chemical composition and heating conditions. Under those circumstances, a change in the maximum temperature is made. These methods have worked well for QD dispersions containing CdSe, CdS, ZnS, InP, InAs, PbS and mixtures thereof.

This document offers a reliable method of determining the mass of a colloidal QD dispersion after removing or decomposing impurities while minimizing potential errors that may otherwise be encountered.

NANOMANUFACTURING –
KEY CONTROL CHARACTERISTICS –

Part 3-2: Luminescent nanoparticles –
Determination of mass of quantum dot dispersion

1 Scope

This part of IEC 62607 specifies a method for determining the mass of a sample of QD dispersion after the removal of impurities and surfactant ligands through heating at high temperatures.

2 Normative references

There are no normative references in this document.

NOTE The Bibliography lists documents that are useful for its application.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

portion

<QD dispersion> small amount of the sample to be analysed that is representative of the concentration of the sample

3.2

dispersing solvent

solvent used to disperse the quantum dots

Note 1 to entry: Ideally, the dispersing solvent has a boiling point between 60 °C and 120 °C.

Note 2 to entry: Common solvents include toluene and hexanes.

4 Apparatus

The apparatus shall consist of the following:

- Hot plate, heat gun, or other heating apparatus for removing dispersing solvent.
- Vacuum line and a chamber to contain the TGA pan for removing dispersing solvent.
- Gas flow for removing dispersing solvent.
- Moderate pressure line (typically < 3,45 kPa) for flow of an inert gas (for example, N_2, Ar, He) over the surface of the dispersing solvent. A sufficient flow shall be maintained to volatilize the solvent, but not so high as to potentially result in spilling the sample from the pan, thus invalidating the measurement.
- Thermogravimetric analysis instrument for performing reliable thermogravimetric analysis.
- TGA pan, typically a small vessel that is compatible with the temperature ranges and design of the thermogravimetric analysis instrument used.
- Syringe or calibrated pipette.

5 Preparation of sample

The TGA pan is tarred. A small portion of the total QD dispersion is drawn into a calibrated syringe or pipette in such a way that the volume can be accurately determined. The total volume of the portion is recorded. The volume of the portion used should result in a dried mass that is within the operating range of the TGA instrument. A small amount of the dispersion is added to the pan. The amount that is added will depend on the size of the TGA pan. The dispersing solvent is evaporated by heating, vacuum or flow of an inert gas. An additional quantity of the dispersion is added to the pan, and the dispersing solvent is evaporated. This process is repeated until the entire portion of the dispersion has been added to the pan and all of the dispersing solvent is removed.

The QD dispersion shall be purified and any unreacted precursors such as Cd and Se shall be removed before TGA sampling. None of the QD mass shall be spilled when filling the pan or removing the solvent.

6 Procedure

6.1 General

The pan with the above prepared sample is placed into the instrument. The measurement in 6.2 shall be performed under an N_2 flow. The nitrogen flow should be made entirely free of oxygen and moisture by using ultra-high purity nitrogen and by adequately purging out the lines and tubing.

6.2 Heating

The sample shall be heated at a ramp rate of 30 °C/min to 5 °C above the boiling point of the dispersing solvent. The pan is held at this temperature for 10 min. The temperature is then increased to 650 °C at a rate of 10 °C/min. The temperature is held at 650 °C for 10 min. The residual mass at this point is the mass of the QD for that volume of dispersing solvent.

The above heating profile is optimal for decomposing and volatilizing common organic impurities while not volatilizing the semiconductor material. Alternate heating profiles may be necessary depending on the nature of the analyte and any inorganic impurities. If an alternative heating profile is used, it shall be included in the test report.

The mass concentration of the dispersion can be calculated by dividing the residual mass by the volume of the portion of the dispersion, as described in 7.1.

An example of this process is included in Annex A.

6.3 Mass concentration of additional samples

Once this test is performed for a standard procedure, the mass concentration of new preparations can be determined from the absorbance spectrum, i.e. the wavelength dependence of the absorbance or optical density or extinction. Mass concentration shall be calculated from the measured absorption spectrum in accordance with 7.2. This calculation shall only be valid for identical preparations. Systems that have process changes shall be measured via TGA to ensure accurate mass concentration determination. The wavelength selected to measure absorbance should be in a region devoid of interference from impurities. Common impurities found in QD synthesis have a low absorbance cross section in the 350 nm to 700 nm range. The portion of the QD dispersion that is analysed should be diluted in a controlled way so that the absorbance is within a linear range of the instrument (typically an absorbance range of 0,2 to 0,8). Additional details can be found in IEC 62607-3-1. An example of this process is included in Annex B.

6.4 Potential instrument errors

6.4.1 Static

As static electricity can result in inconsistent results, any static charge shall be removed from the TGA pan and instrument throughout the operation.

6.4.2 Bumping

As gas is evolved from the sample, non-volatile portions of the sample may spill out of the pan. This process is known as "bumping". This will result in a sudden mass loss. If bumping occurs, the measurement procedure shall be repeated.

NOTE A slower heat ramp decreases the likelihood of bumping.

7 Results and calculations

7.1 Concentration and mass of QDs

$$\mathrm{MC_s} = m_\mathrm{s}/V_\mathrm{s}$$

where

$\mathrm{MC_s}$ is the mass concentration (mg/ml) of sample;

m_s is the residual mass (mg) after procedure;

V_s is the total volume of the portion of the dispersion added to pan (ml); and

$$m_\mathrm{d} = \mathrm{MC_s} \times V_\mathrm{d}$$

where

m_d is the total QD mass of dispersion (mg);

V_d is the total volume of dispersion (ml).

7.2 Mass concentration from relative absorbance

$$\mathrm{MC_n} = \mathrm{MC_i} \times A_\mathrm{n}/A_\mathrm{i}$$

where

$\mathrm{MC_n}$ is the mass concentration of new preparation (ml);

$\mathrm{MC_i}$ is the mass concentration of initial preparation (ml);

A_n is the absorbance of new preparation;

A_i is the absorbance of initial preparation.

8 Measurement uncertainty

Uncertainty of mass measurements can vary widely depending on equipment, experimental conditions and laboratory personnel practices. Users of this document are encouraged to reference IEC/ISO Guide 98-3 for guidance and other related online tools and literature.

In order to provide the proper context for measurements, an estimate of uncertainty should be provided in the test report. Typically, estimates of Type B uncertainties can be included in the test report. The components of uncertainty will vary depending upon the mass measurement technique employed and will change with any modification of the test procedure. Uncertainty estimates shall be reviewed whenever a change in the measurement process is made.

Potential sources of uncertainty include:

- error in volume measurement (will depend on method of measuring volume);
- error in mass measurement (will depend on operating parameters of the specific TGA).

These sources and values of uncertainty shall be reported in the “Estimates of Uncertainty” section of the test report described in Clause 9.

9 Test report

The test report shall include at a minimum, the following information:

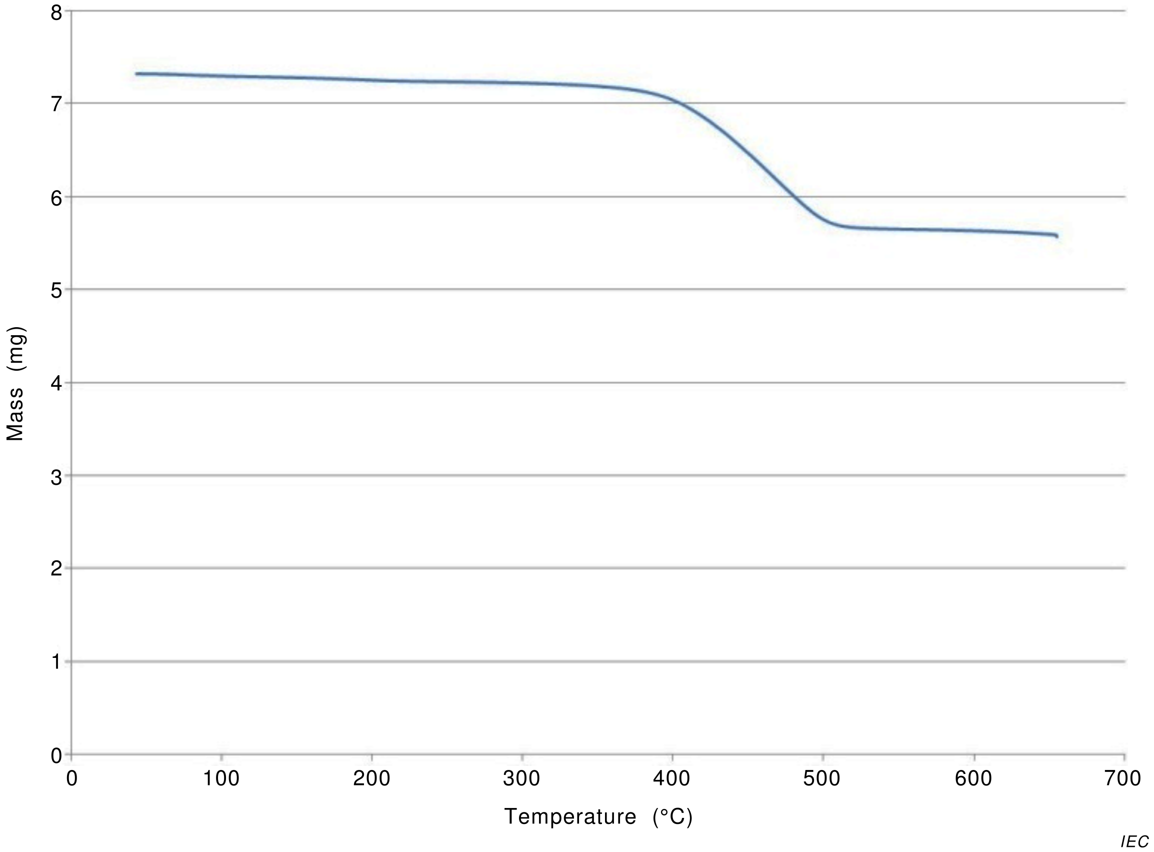
- tare mass of the TGA pan (mg);
- total volume of the portion of dispersing solvent added to the pan;
- residual mass after heating to 650 °C;
- a graph displaying mass vs. temperature of the temperature scan (see Figure A.1);
- total volume of the sample;
- estimates of uncertainty.

Annex A
(informative)

Example of determination of mass of QD dispersion

The following information is applied in this example.

- The total volume of QD dispersion is 20,0 ml.
- 0,200 ml of solution was added to a tarred TGA pan.
- The solvent was removed by heating the TGA pan.
- The dried mass was determined to be 7,3 mg in the instrument.
- After heating, the residual mass was determined to be 5,57 mg.



Mass concentration of QD = 5,57 mg/0,200 ml = 27,9 mg/ml.

Mass of QD in the dispersion = 27,9 mg/ml × 19,8 ml = 552 mg.

Figure A.1 – Mass of QD dispersion vs. temperature

Annex B
(informative)

Determination of mass concentration of additional samples

B.1 General

In this example, Sample A has a known concentration whereas Sample B is an identical preparation but has an unknown concentration.

Sample A was previously determined to have a concentration of 27,9 mg/ml.

B.2 Preparation

Three cuvettes are prepared, a hexane blank, a dilution of sample A (30 µl in 2,97 ml of hexanes) and a dilution of sample B (30 µl in 2,97 ml of hexanes).

B.3 Results and calculations

The absorbance at 350 nm is measured for the two samples. Sample A has an absorbance of 1,21 whereas sample B has an absorbance of 1,43.

The concentration of sample B is calculated by the following formula:

$$27{,}9 \times \frac{1{,}43}{1{,}21} = 33{,}0\,\text{mg/ml}$$

Bibliography

IEC 62607-3-1, *Nanomanufacturing – Key control characteristics – Part 3-1: Luminescent nanomaterials – Quantum efficiency*

IEC/ISO Guide 98-3-2008, *Uncertainty of measurement – Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

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