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Glass sand - Test method for the determination of non-glass inorganic material

Glass sand – Test method for the determination of non-glass inorganic material

The reference procedure defines a method of analysis for the determination of the content of ceramic and inert, i.e. inorganic, non-metallic and non-glass material in glass sand.

The method applies to glass sands, i.e. glass grains less than 1 mm in size.

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INTRODUCTION

This reference procedure UNI/PdR 31:2017 is not a national standard, but is a document published by UNI, provided for by Regulation (EU) No. 1025/2012, which collects provisions relating to shared practices within the following parties signatories of a collaboration agreement with UNI:

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CoReVe – Consorzio Recupero Vetro (Glass Recovery Consortium)
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This reference procedure was drawn up by the “Glass sand sampling” Group, conducted by UNI, consisting of the following experts:

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This reference procedure was ratified by the President of UNI on 11 July 2017.

The reference procedures, adopted exclusively at a national level, are among the “European standardisation deliverables”, as provided for under Regulation (EU) No. 1025/2012, and they are documents that introduce technical requirements, developed on the basis of a rapid process restricted to authors only, under the operational management of UNI.
The reference procedures are available for no more than 5 years. This is the maximum time within which they can be transformed into a standard (UNI, UNI/TS, UNI/TR) after they are published. Otherwise they must be withdrawn.

Following the application of the current reference procedure, anyone who believes that they can offer suggestions to improve it is invited to send their contributions to UNI, the Italian standards agency, for consideration.

SUMMARY

INTRODUCTION

Glass sand (=fines) is used in the production of glass containers as a replacement raw material for waste glass. This is obtained by grinding the small pieces of waste glass together with the waste fraction from the ceramic sorting machines installed at the scrap treatment plants. The grinding can be performed wet or dry.

Commission Regulation (EU) No. 1179/2012 of 10 December 2012, establishing criteria determining when glass cullet ceases to be waste under Directive 2008/98/EC of the European Parliament and of the Council (End-of-Waste Directive), provides that only materials from the collection of glass containers, flat glass and household lead-free glass can be reused in the production of glass (the possibility that raw scrap contains lower quantities than other glass is accepted).

Glass sand is included in these materials.

The End-of-Waste Directive also provides for the limits of acceptability for foreign materials (ceramic, iron, etc.) which must be respected and certified by the manufacturer for each batch of material produced (glass cullet or glass sand).

The acceptance criteria for the Directive are as follows:

a) Ferrous metals:

   50 ppm

b) Non-ferrous metals:

   60 ppm

c) Non-metallic inorganic materials:

   100 ppm of waste larger than 1 mm

   1500 ppm of waste smaller than 1 mm

d) Organic materials

   2000 ppm

For glass sand, the limit to be respected for “non-metallic inorganic materials” is 1500 ppm, this being characterised by a particle size always less than 1 mm.

The End-of-Waste Directive also defines the methods of analysis that must be used at the plant “at appropriate intervals […], representative samples of glass cullet shall be analysed gravimetrically to measure the total non-glass components. The non-glass component content shall be analysed by weighing after mechanical or manual (as appropriate) separation of materials under careful visual inspection”.

This methodology is well suited to the analysis of waste over one millimetre in size, where the material can simply be separated by manual sorting; for material of smaller sizes it is not directly applicable.

This reference procedure has been designed in order to define an analysis method suitable for the latter type of materials and is based on the results of an experimental project developed by the Stazione Sperimentale del Vetro (Experimental Glass Station) at the request of glassware producers of glass packaging and of CoReVe (the Glass Recovery Consortium). The details of the experimental project are described in Appendix A.

1 PURPOSE AND SCOPE OF APPLICATION

This reference procedure defines a method of analysis to determine the content of ceramic and inert materials, i.e. inorganic, non-metallic and non-glass, in glass sand.

The method applies to glass sands, i.e. glass grains less than 1 mm in size. The method of analysis can be applied to glass grains from 1 mm to 5 mm in size.

2 REGULATORY AND LEGISLATIVE REFERENCES

This reference procedure refers to provisions contained in other publications, using dated and non-dated references. These regulatory and legislative references are quoted at appropriate points in the text and are listed below. Regarding the dated references, subsequent changes or revisions made to these publications are only valid if included in this document as an update or revision. For the undated references, the latest edition of the publication to which reference is made is valid.

> Commission Regulation (EU) No. 1179/2012 of 10 December 2012 establishing criteria determining when glass cullet ceases to be waste under Directive 2008/98/EC of the European Parliament and of the Council (End-of-Waste Directive)

3 TERMS AND DEFINITIONS

For the purpose of this document, the following terms and definitions apply:

3.1 glass cullet, secondary raw material: Waste processing product from glass packaging, i.e. glass obtained after removal of materials considered pollutants (plastic, paper, organic material, ceramics, stones, pyroceramic, fragments of leaded glass, fine fragments of screened waste) through suitable washing and selection/removal systems

3.2 glass sand: Materials obtained by crushing glass cullet, secondary raw material and/or from selection in the treatment of glass packaging waste with a final granulometry not exceeding 1 mm

4 PRINCIPLE

The reference procedure defines a method of analysis based on the requirements indicated in Commission Regulation (EU) No. 1179/2012 of 10 December 2012, in which criteria are established for determining when glass cullet intended for the production of glass products, or based on glass by means of re-melting processes, ceases to be waste. In particular, the glass cullet in question, in this case glass sand, ceases to be waste when it falls within the limits defined in Annex 1, Point 1.2 of the aforementioned Regulation.

The limit for non-metallic, inorganic, non-glass material, henceforth defined as “opaque” is fixed at 1500 ppm for material not exceeding 1 mm.

The analysis method described in this reference procedure also incorporates what is described in the aforementioned Annex, in particular the method complies with the following methodological indications:

"(…) At appropriate intervals and subject to review if significant changes in the operating process are made, representative samples of glass cullet shall be analysed gravimetrically to measure the total non-glass components. The non-glass component content shall be analysed by weighing after mechanical or manual (as appropriate) separation of materials under careful visual inspection (…)".

In order to implement what is defined, the method is based on manual separation of the non-glass components present in a representative sample of glass sand, the presence of which is expressed in weight/weight %.

5 INSTRUMENTATION

For the purposes of this analysis method, it is necessary to use the following instruments:

- ASTM 0.600 mm sieve.
- Drying stove capable of reaching at least 120°C.
- Muffle furnace capable of reaching and maintaining the material at 105°C for two hours.
- Scale capable of weighing up to the third decimal place, micrograms.
- Optical stereoscopic microscope with x8 magnification and possibility of illuminating the observation field with transmitted and reflected light.
- Tweezers of suitable size capable of grasping single grains between 0.6 mm and 1 mm.

6 SAMPLING

A representative sample of at least 10 kg of glass sand is reduced by a quarter to about 1 kg. The 1 kg sub-sample must be dried in a stove at 105°C for two hours or by weight constant. The sample is weighed (P1). The material thus treated is sieved using a sieve set at 0.6 mm. The fraction greater than 0.6 mm and less than 1 mm is weighed (P2).

7 ANALYSIS PROCEDURE

An aliquot of 5 g, taken from P2 and weighed with a balance of appropriate precision up to the third decimal digit (micrograms), is submitted for separation of the opaque materials under the optical stereoscopic microscope (P3).

For the separation of the opaque materials under the microscope from a 5 g sample, a suitable quantity of sample (a few tenths of grams at a time) is placed under the optical stereoscopic microscope at x8 magnification. The lighting must be such as to enable opaque bodies to be recognised and distinguished from coloured transparent glass. It is recommended to use full reflected light for discriminating between opaque and coloured transparent grains, while the light

transmitted must be adjusted according to the needs of a trained operator, so that the opacity of the material can be assessed but at the same time ensure comfortable viewing.

The nature of grains of so-called opaline glass, visually opaque but glassy in nature and so comparable to coloured transparent glass, must be assessed by observing the translucency of the grain itself in the reflected light.

The material recognised as opaque is separated with tweezers of an appropriate size to enable a grain measuring between 0.6 mm and 1 mm to be grasped. The separated material is placed in a separate container.

8 DETERMINATION OF THE CONTENT OF OPAQUE MATERIAL (NON-GLASS)

The operations described in Point 7 must be repeated until the weighed 5 g are used up.

The separated opaque material from the 5 g is weighed (P4). The calculation of the content of opaque material is made using the following formula:

$$opaque\ ppm\ = \frac{P4 \times P2}{P3 \times P1} \times 10^6$$

9 ASSESSMENT OF THE UNCERTAINTY IN MEASUREMENT

In order to determine the uncertainty of the method a series of measurements (31) was repeated on the same batch of material by different operators.

The statistical descriptors calculated are reported below:

- average value = 2662 ppm
- degrees of freedom = 30
- deviation (standard deviation) = 289 ppm
- average deviation = 52 ppm
- relative mean deviation = 0.0195

In this case the relative mean deviation corresponds to the expanded combined uncertainty *Uc(rel)*, since the uncertainty related to the weighing error is negligible compared to the uncertainty of the analysis. The Student's t-test for 30 degrees of freedom has a value of *t(stud)* = 2.75 for a cover factor of 99%.

The relative expanded uncertainty Ue(rel) is thus obtained as:

Ue(rel) = Uc(rel) x t(stud) = 0.0195 x 2.75 = 0.054

The expanded uncertainty Ue is obtained by multiplying the relative expanded uncertainty by the average value of the concentration:

Ue = 2662 x 0.054 = 143 ppm

PLEASE NOTE: In order to maintain the reliability of the measurement, it is suggested to perform an inter-laboratory test each year, or at each change of operator or instrumentation or elements of it, to verify the effectiveness of the recognition of the materials by the operator.

ANNEX A – DESCRIPTION OF THE EXPERIMENTAL GLASS STATION'S EXPERIMENTAL PROJECT

A.1 INTRODUCTION

The aim of the project developed by the Experimental Glass Station, which has led to the definition of the method described in this reference procedure, has had the purpose of defining a glass sand analysis method which:

- would allow a comparison between the limit value established for the non-metallic inorganic materials in Annex 1, Point 1.2, of the End-of-Waste Directive (criteria column);
- complied with the requirements for analysis in Annex 1, Point 1.2 of the End-of-Waste Directive (column for minimal internal monitoring obligations);
- was applicable at sustainable cost and with acceptable delivery times;
- was sufficiently robust, repeatable and reproducible.

The project was developed in according to the following stages:

- preliminary sampling and characterisation;
- definition and drafting of the analysis method;
- characterisation of the materials according to the identified method;
- repeatability and reproducibility of the method.

A.2 PRELIMINARY SAMPLING AND CHARACTERISATION

At this stage glass sand samples were taken at the principal national producers.

About 20 kg sand are sampled at each plant for each type produced (hypothetically glass sand for separating ceramic materials and glass sand for separating fine glass). At the same time as sampling, data were collected, where available, useful for understanding the process and identifying factors affecting the final ceramic concentration.

A.3 DEFINITION AND DRAFTING OF THE ANALYSIS METHOD

From the observations made during the sampling and the experience of the Experimental Glass Station in the field of glassy, ceramic and inert materials, it became evident that for the assessment of the presence of "non-glassy material" in glass sand it was not possible to apply the same product evaluation as for the glass cullet, such as for example the visual control about 50 kg of material.

During the project, the analytic techniques to be used in the quantitative and gravimetric determination of the non-glassy opaque materials in the glass sand were considered. From these analyses it emerged that the separation technique using heavy liquids, which uses the difference in density of the various materials of which the glass sand is made to separate them accordingly, while it allows a gravimetric evaluation of the separated materials, it is not able to distinguish

opaque ceramic material from glass, both very similar in density; moreover, it recognises lead glass, non-opaque as is well known, as a heavy material, so this technique lacks selectivity.

The technique based on melting a sample of glass sand for brief periods, under appropriate conditions, allows the formation of a sample of transparent glass in which the particles of opaque materials present can easily be distinguished. However, despite the simple identification of opaque bodies (infused) in the glass sample, in this case the technique does not enable them to be assessed gravimetrically, as it is not possible to weigh the infused bodies if encased in molten glass.

The definition of the method described in this procedure was therefore reached, which was applied to samples of glass sand from various producers, and it also resulted applicable to glass sand of various origins. During the tests it was noted that the method can be used to assess any improvements in the process by monitoring. It was also noted that the variability in the granulometric curve notably affects the calculated final value.

A.4 CHARACTERISATION OF THE MATERIALS ACCORDING TO THE IDENTIFIED METHOD

The method described, identified in the definition and drafting of the analysis method described in Point A.3, was applied to non-commercial glass sand samples characterised by high values of ceramic provided by the five companies visited. The aim of the test was to verify the applicability of the method, particularly for high values of opaque materials.

On four samples it was possible to repeat the procedure following changes in the production process, aimed at improving the quality of the glass sand as measured by this test method. The objective, in this case, was to verify how reactive the method was in regard to specific variations in the production process.

Finally, as a part of the experimental project, the method was shared with an External Laboratory (Istituto di Geoscienze e Georisorse, CNR) (Institute of Geosciences and Earth Resources, National Research Council of Italy). The results obtained from the External Laboratory are comparable to those obtained from the Experimental Glass Station, in terms of repeatability and reproducibility.

A.5 REPEATABILITY AND REPRODUCIBILITY OF THE METHOD

A.5.1 REPEATABILITY

The repeatability of the value measured within the same batch of glass sand strongly depends on the quantity of material screened.

To identify the minimum quantity of material to be analysed, different quantities of glass sand were screened, treated as described in the previous Point A.4, repeating the operation an appropriate number of times. The variation of the average value is shown in Figure A.1.

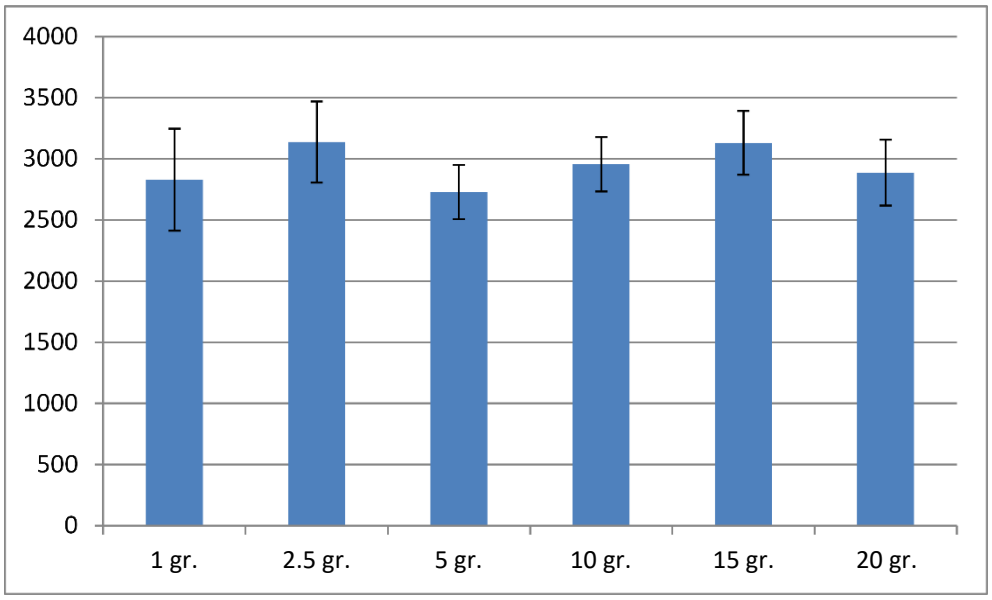

Figure A.1 – Ppm value in relation to the quantity of material analysed for the same sample

In the chart below in Figure A.2, the expanded uncertainty trend (k=2) is shown associated with analysis performed on different quantities of material as a percentage of their average value.

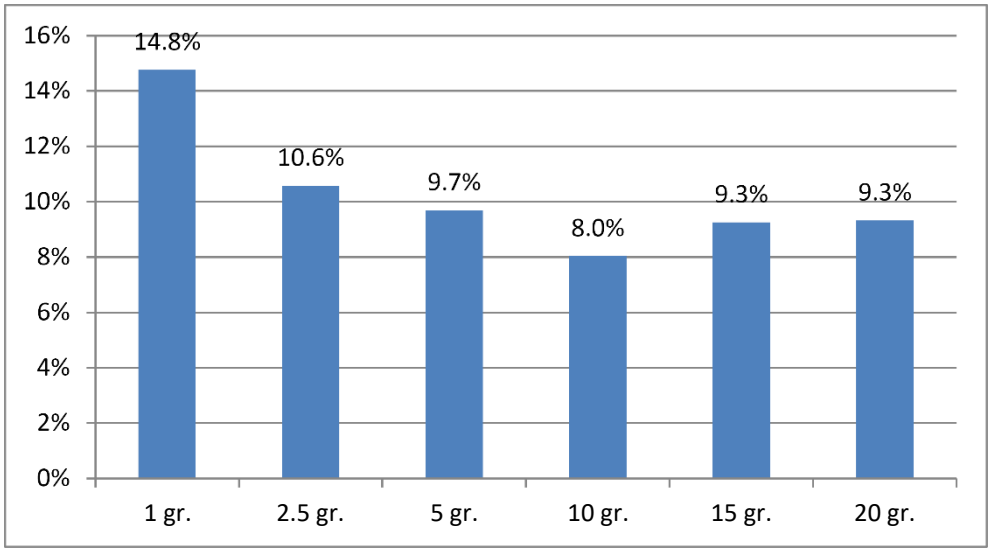

Figure A.2 – Expanded uncertainty trend (as a percentage of the average value) regarding the quantity of sample analysed

From analysis of the results it can be seen that for quantities of glass sand greater than 5 g the expanded uncertainty remains fairly constant. This value was therefore taken as a minimum quantity of glass sand to be analysed.

A.5.2 REPRODUCIBILITY

To calculate the uncertainty associated with different operators a single glass sand sample was analysed from three different operators previously trained and named Op. 1, Op. 2 and Op.3.

In Table A.1 the average values and the standard deviation for each operator are reported, compared with the totals.

	Op. 1	Op. 2	Op. 3	total
mean	2445	2647	2842	2650
std dev	235	195	282	287

Table A.1 – Reproducibility test statistics

In Figure A.3 the uncertainty associated with the mean (standard deviation), expressed in ppm associated with each individual operator, for the same number of tests performed. Considering that the average value of opaque ceramic non-glass material is 2650 ppm, the uncertainty associated with the operators is somewhat reduced (less than 5%). This result demonstrates the good reproducibility of the method.

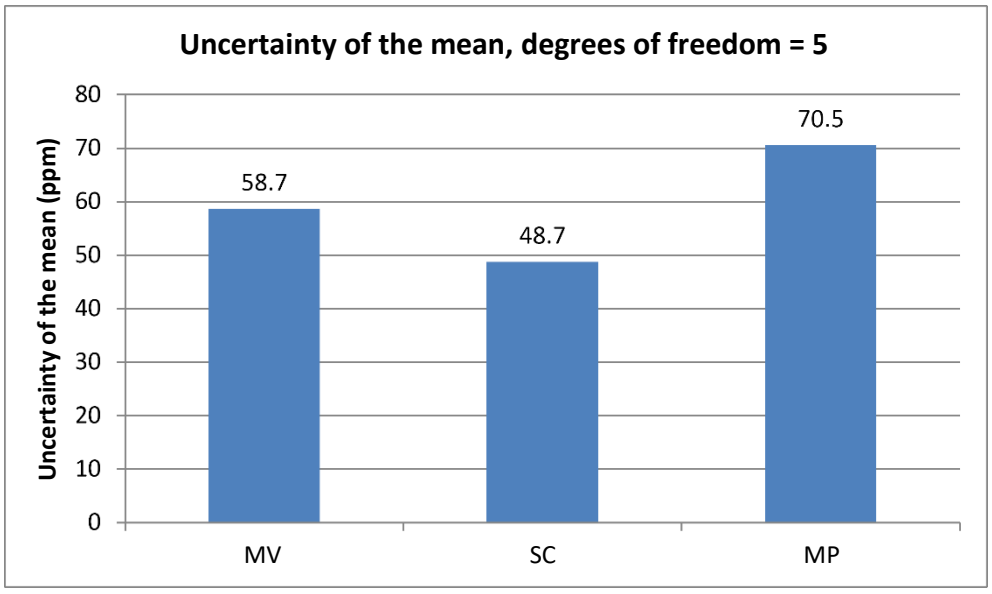

Figure A.3 – Uncertainty of the mean for the three different operators

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