International Standard 4104

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Dental zinc polycarboxylate cements

Ciments dentaires au polycarboxylate de zinc

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Dental zinc polycarboxylate cements

0 Introduction

This International Standard covers one of the main types of cement used in dentistry, the others being zinc phosphate (see ISO 1566), zinc oxide/eugenol (see ISO 3106 and ISO 3107), and silicate/silico-phosphate (see ISO 1565 and ISO 3851).

In preparing this International Standard, ISO/TC 106, has, wherever possible, adopted the appropriate test techniques from the related International Standards concerning cements. Carboxylate cements do, however, have a number of unique properties and it has consequently been necessary for some new test methods to be introduced. Experience in the use of these test methods will, with other relevant technical considerations, form the basis for any future revision or amendment of this International Standard.

1 Scope and field of application

This International Standard specifies requirements for dental zinc polycarboxylate cements the principal constituents of which are zinc oxide and aqueous solutions of polyacrylic acid or similar polycarboxylic compounds, or zinc oxide-polycarboxylic acid powders to be mixed with water.

The cements covered by this International Standard are those used for joining or sealing appliances to oral structures or to other appliances, or to serve as a base or foundation for other filling materials or to serve as a temporary filling material.

2 References

ISO 2590, *General method for the determination of arsenic — Silver diethyldithiocarbamate photometric method.*

ISO/TR 7405, *Biological evaluation of dental materials.*

3 Classification

The cements covered by this specification shall be classified as follows :

- **Type 1 :** Luting material
- **Type 2 :** Filling material

4 Requirements

4.1 Material

The cement components shall consist of a powder and a liquid which, when mixed according to the manufacturer's instructions, will set to a condition suitable for its intended dental use.

4.2 Components

4.2.1 Liquid

The liquid shall be clear and there shall be no deposit or sediment inside the container. It shall be sufficiently free flowing for clinical use.

4.2.2 Powder

The powder shall be free from extraneous material such as dirt or lint. The pigment, if any, shall be uniformly dispersed throughout the powder.

4.3 Unset cement

The cement, when mixed according to the manufacturer's instructions, shall be of a uniformly smooth consistency, completely mixed and shall not evolve gases.

4.4 Set cement

4.4.1 Acid-soluble arsenic content

The acid-soluble arsenic content of the set cement shall be not more than 2 ppm when the sample is prepared in accordance with 6.8 and the arsenic content determined by the procedure specified in ISO 2590. An alternative recognized analytical method of adequate sensitivity may be used, although, in cases of dispute, ISO 2590 shall be the referee method.

4.4.2 Physical requirements

The requirements for manipulation time, setting time, compressive strength, diametral tensile strength, water-leachable material content, film thickness, and maximum arsenic content, shall be as detailed in the table when tested according to clause 6.

4.5 *Freedom from toxicity*

The mixed material, when used in accordance with the instructions to be provided by the manufacturer, shall neither cause prolonged damage to oral tissues, nor have any adverse systemic effect.

NOTE — Specific toxicity tests are given in ISO/TR 7405.

4.6 Instructions to be provided by the manufacturer

Instructions for proportioning and manipulating the cement shall include the following details :

a) information regarding the mixing temperature and its effects, the nature of the slab or pad and of the spatula to be used;

b) the powder/liquid ratio (stated as a mass : mass ratio, in grams of powder per gram of liquid); and a recommended technique for dispensing this powder/liquid ratio;

c) the rate of incorporation of the powder into the liquid;

d) the time of mixing;

e) the minimum satisfactory manipulation time after the end of mixing, including conditions required for testing.

5 Sampling and inspection

5.1 Sampling

The method of procurement of a suitable sample shall be the subject of an agreement between the interested parties. A test sample shall consist of one or more retail packages from the same batch, containing sufficient material to carry out the tests plus an allowance for repeats, if necessary.

5.2 Inspection

Visual inspection, using a X 10 magnifier, shall be used in determining compliance with the requirements outlined in 4.2.1 and 4.2.2.

6 Test methods

6.1 Preparation of test specimens

6.1.1 Conditioning

Unless otherwise stated, all specimens shall be prepared at 23 ± 1 °C and at a relative humidity of 50 ± 5 %.

6.1.2 Apparatus for mixing

6.1.2.1 Mixing slab as specified by the manufacturer in 4.6a).

6.1.2.2 Spatula, made from a material not affected by the cement as specified in 4.6a).

Ensure that all instruments and apparatus used in mixing and testing the cements are clean, dry, and free from particles of hardened cement.

Before commencing mixing the cement, bring all the apparatus and equipment to the conditions specified in 6.1.1.

6.1.3 Method of mixing

Place the correct quantities of powder and liquid, using the powder/liquid ratio as stated in the manufacturer's instructions, on the mixing slab (6.1.2.1).

Mix the material in accordance with the manufacturer's instructions.

Do not allow any powder or liquid to remain on the mixing slab when mixing has been completed.

6.1.4 *Powder/liquid ratio for testing*

The powder/liquid ratio stated in the manufacturer's instructions [see 4.6 b)] shall be used for all testing procedures in this International Standard.

Table — Physical requirements

Type	Minimum manipulation time	Maximum setting time	Minimum compressive strength	Minimum tensile strength	Maximum water-leachable material content	Maximum film thickness	Maximum arsenic content
	minutes	minutes	MPa	MPa	$S \cdot m^{-1}\ kg^{-1}$	µm	ppm
1	1,5	9,0	50	6	40	25	2,0
2	1,5	5,0	50	6	40	—	2,0

NOTE — Both the manipulation time and setting time are measured from the end of the mixing time (setting time is usually measured from the start of mixing).

6.2 Manipulation time

6.2.1 Apparatus

6.2.1.1 Polished glass slab, approximately 150 mm long × 75 mm wide × 20 mm thick.

6.2.1.2 Spatula, made from a material not attacked or corroded by the cement.

6.2.1.3 Two flat glass plates, each 50 mm square and approximately 3 mm thick.

6.2.1.4 A **dispensing device** consisting of a glass tube and a polytetrafluoroethylene (PTFE) plunger, to deliver 0,5 ml of mixed cement in the form of a cylinder 6 mm high and 10 mm in diameter.

6.2.1.5 A **100 g mass,** or equivalent loading device.

6.2.1.6 Stopwatch.

6.2.2 Procedure

Place on one glass plate (6.2.1.3) 0,5 ml of the mixed cement from the dispensing device (6.2.1.4). One minute after completion of mixing place the other glass plate (6.2.1.3) on top followed by the application of the mass of 100 g (6.2.1.5). Remove the load 10 min after the start of mixing and measure the disc diameter as the average of at least two measurements at 90° to each other. Continue trials at least in triplicate at increases of 30 s intervals until the disc diameter is reduced by 10 % or more from the diameter obtained from the first test at 1 min after the completion of mixing.

Determine the manipulation time as the time elapsed from the end of mixing to the time at which the application of the load results in a reduction of disc diameter by 10 % from the diameter obtained from the first test at 1 min after the completion of mixing.

6.3 Setting time

6.3.1 Apparatus

6.3.1.1 Cabinet capable of being controlled at 37 ± 1 °C and a relative humidity of at least 30 %.

6.3.1.2 Indentor, of mass 400 ± 1 g, having a flat end of diameter 1,0 ± 0,1 mm. The needle tip shall be cylindrical for a distance of approximately 5,0 mm. The needle end shall be plane and at right angles to the axis of the rod.

6.3.1.3 Metal moulds as illustrated in figure 1.

6.3.1.4 Metal block of minimum dimensions 8 mm × 20 mm × 10 mm, either as part of 6.3.1.1 or 6.3.1.2 or as a separate item.

6.3.1.5 Aluminium foil.

6.3.2 Procedure

Place the mould (6.3.1.3) conditioned to 23 ± 1 °C on a piece of the aluminium foil (6.3.1.5) of convenient size and fill to a level surface with cement.

One minute after completing the mix, place the assembly containing the specimen on the metal block (6.3.1.4), which has been conditioned to 37 ± 1 °C in the cabinet (6.3.1.1) and replace the block, mould and specimen in the cabinet. One and a half minutes after completing the mix, carefully lower the indentor (6.3.1.2) vertically onto the surface of the cement and allow to remain there for 5 s. Repeat this operation at 30 s intervals until near the expected time of setting, at which stage it should be carried out at 15 s intervals. Maintain the needle in a clean condition by cleaning, if necessary, between indentations. A trial run may be necessary for determining the approximate setting time.

Record the setting time as the period of time which elapses from the completion of mixing to the time when the needle fails to make a perceptible circular indentation on the surface of the cement, when viewed under a hand lens of magnification X 2.

Make three such tests and determine the mean, rounded up to the nearest 15 s.

6.4 Compressive strength

6.4.1 Apparatus

6.4.1.1 Water bath at 37 ± 1 °C or cabinet capable of being controlled at 37 ± 1 °C and a relative humidity of 90 to 100 %.

6.4.1.2 Split moulds and plates such as those shown in figure 2, of internal height 6,0 ± 0,1 mm and internal diameter 4,0 ± 0,1 mm, made of stainless steel or other suitable material that will not be attacked or corroded by the cement.

NOTE — To facilitate the removal of the hardened cement specimen, the internal surface of the moulds and plates should be evenly coated, prior to filling, with a 3 % solution of micro-crystalline or paraffin wax in pure toluene. Alternatively, a thin film of silicone grease or PTFE dry film lubricant may be used.

6.4.1.3 Individual screw clamps such as those shown in figure 2.

6.4.1.4 Compressive strength testing apparatus having a cross-head speed of 1 mm/min.

6.4.1.5 Filter paper.

6.4.1.6 Micrometer or similar measuring instrument, accurate to 10 µm.

6.4.2 Preparation of test specimens

Condition the moulds (6.4.1.2), screw clamps (6.4.1.3), and top and bottom plates (6.4.1.2) at 23 ± 1 °C. After mixing in accordance with the manufacturer's instructions, pack the cement, to a slight excess, into the split mould within 1 min of the completion of mixing.

NOTE — In order to consolidate the cement and avoid trapping air, it is advisable to convey the largest convenient portions of mixed cement to the mould and apply to one side with a suitable instrument. Fill the mould to excess in this manner and then place on the bottom plate with some pressure.

Remove any bulk extruded cement, place the top metal plate in position and manually squeeze together. Put the moulds and plates in the clamp and screw tightly together. Not later than 2 min after the completion of mixing, transfer the whole assembly to the water bath or cabinet (6.4.1.1), controlled at 37 ± 1 °C and 90 to 100 % relative humidity.

One hour after the completion of mixing, remove the plates and surface the ends of the specimen plane, at right angles to its long axis.

Grind the ends flat and remove any excess cement by drawing back and forth on a glass plate with a small amount of 45 µm (350 mesh) silicon carbide powder mixed with water, or equivalent waterproof silicon carbide abrasive paper. Keep both ends of the specimen wet during the grinding and rotate about one-quarter turn every few strokes.

Remove the specimen from the mould immediately after surfacing and rapidly check for air voids or chipped edges. Discard any such defective specimens.

Immerse each acceptable specimen in distilled water or water of an equivalent purity and maintain at 37 ± 1 °C for 23 h.

6.4.3 Procedure

Twenty-four hours after the completion of mixing, determine the compressive strength of the test specimens in the following manner using the testing apparatus (6.4.1.4) at a cross-head speed of 1 mm/min.

Measure the diameter of the test specimen using a suitable micrometer (6.4.1.6).

Place the specimen with the flat ends covered with a piece of wet filter paper (6.4.1.5) between the platens of the testing apparatus so the load is applied in the long axis of the specimen.

Record the maximum load applied when the specimen fractures.

6.4.4 Expression of results

Calculate the compressive strength, P, in megapascals, using the formula:

$$P = \frac{4\,F}{\pi\,D^2}$$

where

F is the maximum applied load, in newtons;

D is the diameter of the specimen, in millimetres.

Carry out five determinations.

If all five, or four out of the five, results obtained are below the appropriate limit listed in the table, the material shall be deemed to have failed the test. If all five or four out of the five results obtained are above the appropriate limit listed in the table, the material shall be deemed to have passed the test. In other cases, prepare a further ten specimens and obtain the median result for all fifteen specimens. Round up this value to the nearest two significant figures and record as the compressive strength.

6.5 Diametral tensile strength

6.5.1 Apparatus

As detailed in 6.4.1.

6.5.2 Preparation of test specimens

As detailed in 6.4.2.

6.5.3 Procedure

Twenty-four hours after the completion of mixing, determine the tensile strength of the test specimens in the following manner, using the testing apparatus (6.4.1.4) at a cross-head speed of 1 mm/min.

Measure the diameter and length of the test specimen using a suitable micrometer (6.4.1.6).

Place the specimen with the diametral surfaces covered with a piece of wet filter paper between the platens of the testing apparatus so that the load is applied in the short axis of the specimen.

Record the maximum load applied when the specimen fractures.

6.5.4 Expression of results

Calculate the tensile strength, T, in megapascals, using the formula

$$T = \frac{2\,F}{\pi\,l\,D}$$

where

F is the maximum applied load, in newtons;

D is the diameter of the specimen, in millimetres;

l is the length of the specimen, in millimetres.

Carry out five determinations.

If all five or four out of the five results obtained are below the appropriate limit listed in the table, the material shall be deemed to have failed the test. If all five or four out of the five results obtained are above the appropriate limit listed in the table, the material shall be deemed to have passed the test. In other cases, prepare a further ten specimens and obtain the median result for all fifteen specimens. Round up this value to the nearest two significant figures and record as the diametral tensile strength.

6.6 Film thickness (Type 1 cements only)

6.6.1 Apparatus

6.6.1.1 Two optically flat round glass plates of minimum uniform thickness 5 mm, having a contact area of 200 ± 10 mm^2.

6.6.1.2 Loading device, such as that shown in figure 3, to apply a load of mass 15 kg on the anvils.

6.6.1.3 Micrometer or similar measuring instrument, accurate to 1 µm.

6.6.2 Procedure

Measure the combined thickness of the two glass plates (6.6.1.1) in contact to an accuracy of 1 µm.

Deposit a sufficient (approximately 0,1 ml) quantity of cement, mixed as described in 6.1, to cover the plate on the centre of one of the glass plates (6.6.1.1). Place the second glass plate centrally on this cement.

One and a half minutes after completing mixing, carefully apply, by means of the loading device (6.6.1.2), a load of mass 15 kg vertically on the top plate and leave for 7 min. It is essential to ensure that the cement completely fills the area between the two glass plates. Ten minutes after the commencement of mixing, measure the thickness of the two glass plates and the cement film, using the micrometer (6.6.1.3).

Calculate the difference in the thickness of the plate with and without the cement film and record this as the thickness of the film. Report the mean of three such tests to the nearest 5 µm.

6.7 Water-leachable material content

Carry out the determination in duplicate.

6.7.1 Apparatus

6.7.1.1 Cabinet, capable of being controlled at 37 ± 1 °C and a relative humidity of 90 to 100 %.

6.7.1.2 Mould, consisting of a split brass or stainless steel ring contained in a former or retaining ring as illustrated in figure 4. The height of the ring shall be 1,0 ± 0,03 mm and the internal diameter 10 ± 0,3 mm.

6.7.1.3 Individual screw clamps.

6.7.1.4 Platinum wire, thread or unwaxed dental floss.

6.7.1.5 Two wide mouthed polyethylene bottles of approximately 50 ml capacity, as illustrated in figure 5.

6.7.1.6 Wheatstone bridge.

6.7.1.7 Conductivity cell, consisting of two platinum electrodes approximately 15 mm in diameter and mounted parallel to each other 7 mm apart.

6.7.1.8 Thin sheets of polyethylene or cellulose acetate.

6.7.1.9 Flat metal or glass plate.

6.7.2 Reagent

Potassium chloride, standard solution, $c(\text{KCl}) = 0{,}1$ mol/l. Dissolve 7,455 g of potassium chloride of analytical grade in 1 000 ml of distilled water or water of equivalent purity.

6.7.3 Preparation of the test specimen

Place the mould (6.7.1.2) on a thin polyethylene or cellulose acetate sheet (6.7.1.8) backed by a flat plate (6.7.1.9). Insert a convenient tared length of wire or dental floss through the split ring so that at least 4 mm projects into the ring. Fill the split ring with cement mixed as described in 6.1.

Cover with a further plate faced with a sheet of polyethylene or cellulose acetate, press firmly together and apply the screw clamp.

Two minutes after the completion of mixing, place the mould, plates and the screw clamp into the cabinet (6.7.1.1).

After 1 h, remove the plates and polyethylene or cellulose acetate sheets from the clamp and carefully separate the cement disc and attached wire or dental floss from the split ring. Remove any surplus cement from the edge of the disc and lightly brush the surface to remove any loose material. Prepare two such specimens.

6.7.4 Preparation of test solution

Weigh the two prepared specimens immediately and suspend, by means of the wire or unwaxed dental floss, in 40,0 ml of water contained in the polyethylene bottle (6.7.1.5). Ensure that the specimen only just touches the side of the bottle. Close the lid as tightly as possible and store for 23 h at 37 ± 1 °C.

6.7.5 Procedure

Remove the specimens from the bottle. Immerse the conductivity cell in the test solution (40,0 ml) and measure the electrical conductance G. Record the conductance, G_o, of distilled water [after storage at 37 °C for 24 h in a polyethylene bottle (6.7.1.5)]. Measure the conductance, G_s, of the standard potassium chloride solution. Make all determinations of conductance at 23 ± 1 °C.

Calculate the cell constant, K, in metres to the power of minus one, using the literature value of specific conductance of 0,1 mol/l potassium chloride solution at 23 °C (i.e. 1,239 $S \cdot m^{-1}$) in the formula :

$$K = \frac{1{,}239}{G_s - G_o}$$

Convert the conductance reading for the test solution to a specific conductance value in Siemens per metre ($S \cdot m^{-1}$) using the equation for specific conductance :

$$\sigma = K (G - G_o)$$

This specific conductance, σ, should be divided by the mass of the sample to give a conductivity value in Siemens per metre per gram ($S \cdot m^{-1} \cdot g^{-1}$) which is then multiplied by 1 000 to give the result in the recognized S.I. units of Siemens per metre per kilogram.

6.8 Acid-soluble arsenic content

6.8.1 Preparation of sample

Powder the set cement and sieve through a 75 µm (200 mesh) sieve. Disperse 2 g of the sieved powder in 40 ml of water and add 10 ml of hydrochloric acid (35 % m/m, 1,18 g/ml). Use this solution for the determination of the acid-soluble arsenic content.

6.8.2 Procedure

Use the method specified in ISO 2590.

7 Packaging and marking

7.1 Package

The components shall be supplied in securely sealed containers[1] made from materials which neither react with, nor permit contamination of, the contents.

7.2 Instructions for use

Instructions for proportioning and handling the powder and liquid shall accompany each package.

7.3 Marking containers

Each container shall be clearly marked with the following particulars :

a) the name and/or trademark of the manufacturer and classification type of cement;

b) a serial number or code and the date of manufacture for that particular lot of cement powder or liquid;

c) the minimum net mass, in grams, of the powder and the liquid, as appropriate;

d) the number of this International Standard, i.e. ISO 4104;

e) for capsulated materials, where the manufacturer supplies different materials or quantities of the same type of capsule, each capsule shall be suitably coded to indicate its contents;

f) recommended storage conditions.

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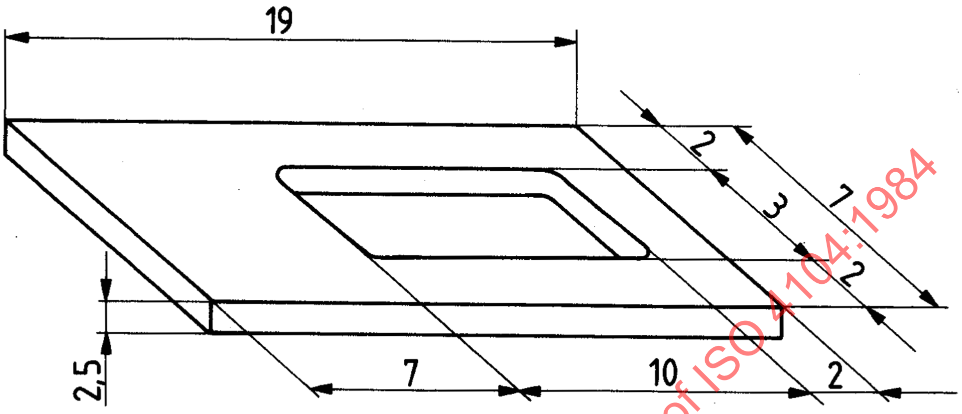
[1] For the purpose of this International Standard, the container shall be considered to be the immediate wrapping of the component.

Dimensions in millimetres



Internal corners may be rounded

Figure 1 — Mould for use in determining setting time

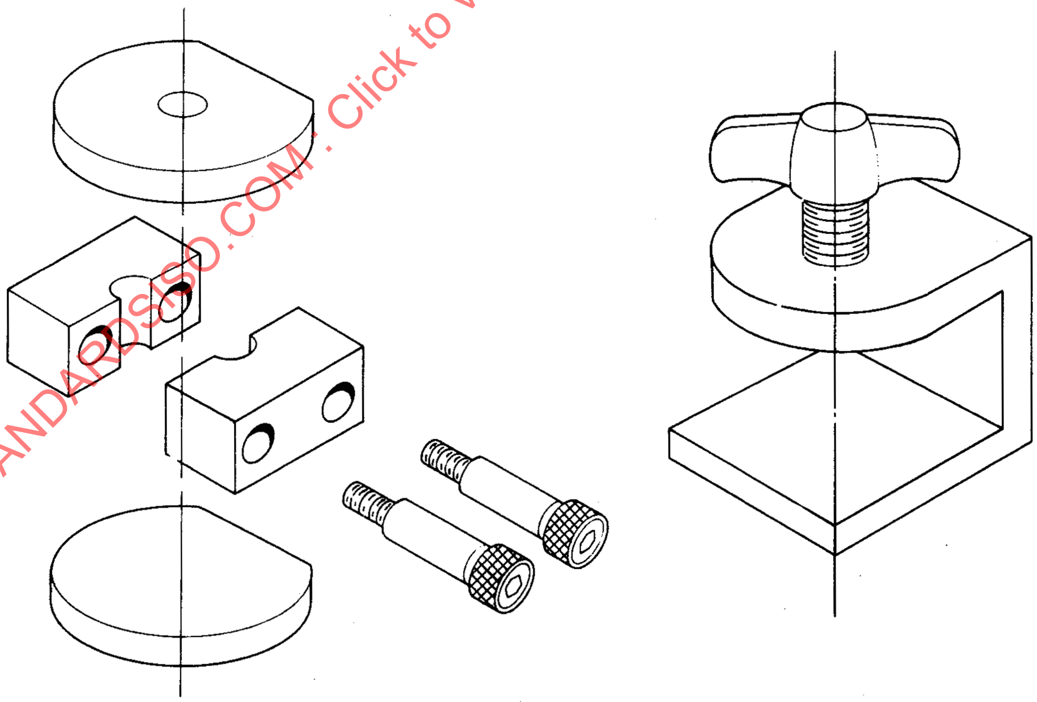


Figure 2 — Mould and clamp for preparation of compressive test specimen