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NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 43011-2023

Paper, board and paper products - Determination of chloropropanol content

纸、纸板和纸制品 氯丙醇含量的测定

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1 Scope

GB/T 43011-2023 gives the determination of chloropropanols in paper, board and paper products. The compounds concerned - 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol - are not added deliberately: they are residues of the polyamidoamine-epichlorohydrin wet strength resins that let a paper towel or a tea bag hold together when wet, and both are classed as probable carcinogens, which is why food contact paper is limited on them. The standard describes the principle, the reagents and materials, the apparatus, the analytical procedure by GC-MS, the calculation of results, the precision, the detection and quantitation limits and the test report, with an informative annex giving the chromatograms and mass spectra of the two analytes. It took effect on 1 April 2024.

This document describes a method for the determination of content of 1,3-dichloro-2-propanol (1,3-DCP) and 3-chloro-1,2-propanediol (3-MCPD) in paper, board and paper products. This document is applicable to all kinds of paper, board and paper products; is used as a reference for pulps and papermaking wet strength agents.

2 Normative references

The contents of the following documents, through normative references in this text, constitute indispensable provisions of this document. Among them, for dated references, only the edition corresponding to that date applies to this document. For undated references, the latest edition (including all amendments) applies to this document.

GB/T 462 Paper, board and pulps - Determination of moisture content of analytical sample

GB/T 6682 Water for analytical laboratory use - Specification and test methods

3 Terms and definitions

There are no terms or definitions to be defined in this document.

4 Principle

After the sample is chopped, mixed or diluted, add a deuterium-labeled internal standard solution to the specimen; use sodium chloride solution (20%) to extract it. After concentration, use heptafluorobutyrylimidazole to derivatize it; use gas chromatography-mass spectrometry for detection AND the internal standard method for quantification.

5 Reagents and materials

Unless otherwise specified, use only analytically pure reagents.

6.7 Nylon microporous filter membrane: Pore size is 0.22 μm.

6.8 Vortex mixer.

6.9 Pipette: 100 μL and 1000 μL.

6.10 Other commonly-used laboratory glassware.

7.1 Preparation of standard solutions

7.1.1 Chloropropanol mixed standard stock solution (1000 mg/L): Respectively weigh 50 mg (accurate to

0.1 mg) of 1,3-DCP standard (5.9) and of 3-MCPD standard (5.10); use ethyl acetate (5.3) to dissolve and transfer to a 50 mL volumetric flask; use ethyl acetate (5.3) to dilute to the mark; seal and store at 0 °C~4 °C. The storage period is 6 months.

7.1.2 Chloropropanol mixed standard intermediate solution (10 mg/L): Accurately pipette

0.1 mL of chloropropanol mixed standard stock solution (7.1.1) into a 10 mL volumetric flask; use ethyl acetate (5.3) to dilute to the mark; seal and store at 0 °C~4 °C. The storage

period is 3 months.

7.1.3 Chloropropanol mixed standard intermediate solution (1 mg/L): Accurately pipette

0.1 mL of chloropropanol mixed standard stock solution (7.1.1) into a 100 mL volumetric flask; use ethyl acetate (5.3) to dilute to the mark; seal and store at 0 °C~4 °C. The storage period is 3 months.

7.1.4 Chloropropanol internal standard mixed standard stock solution (1000 mg/L): Respectively weigh 50 mg (accurate to

0.1 mg) of 1,3-DCP-D5 standard (5.11) and of 3-MCPD-D5 standard (5.12); use ethyl acetate (5.3) to dissolve and transfer to a 50 mL volumetric flask; use ethyl acetate (5.3) to dilute to the mark; seal and store at 0 °C~4 °C. The storage period is 6 months.

7.1.5 Chloropropanol internal standard mixed standard intermediate solution (10 mg/L): Accurately pipette

0.1 mL of chloropropanol internal standard mixed standard stock solution (7.1.4) into a 10 mL volumetric flask; use ethyl acetate (5.3) to dilute to the mark; seal and store at 0 °C~4 °C. The storage period is 3 months.

7.1.6 Chloropropanol standard working solutions: Respectively pipette

0.01 mL,

0.05 mL,

0.1 mL,

0.2 mL,

0.4 mL,

0.8 mL,

1.6 mL of chloropropanol mixed standard intermediate solution (1 mg/L) (7.1.3) AND

0.32 mL of chloropropanol mixed standard intermediate solution (10 mg/L) (7.1.2) INTO transparent glass tubes with a stopper (cap) of appropriate volume (5 mL or 10 mL) with good airtightness. Respectively add 20 µL of chloropropanol internal standard mixed standard intermediate solution (10 mg/L) (7.1.5); add n-hexane (5.2) to 2 mL and mix well. Prepare a series of standard working solutions containing 10 ng, 50 ng, 100 ng, 200 ng, 400 ng, 800 ng, 1600 ng, and 3200 ng of 1,3-DCP and 3-MCPD respectively; in which the mass of each deuterated chloropropanol is 200 ng. Standard solutions of other concentrations can also be prepared as needed. Prepare the standard working solution at the time of use.

7.2 Sample processing For the sample of paper, board, paper products and pulp, weigh about 10 g of the sample; cut it into small pieces of about 5 mmx5 mm. After mixing well, accurately weigh

1.0 g (accurate to 0.0001

g) of the specimen into a glass test tube (6.5). At the same time, take another specimen from the sample; measure the moisture content according to GB/T 462. For the sample of papermaking wet strength agents, if the chloropropanol content is high, in order to ensure the representativeness of the sampling, use water (5.1) to dilute the sample appropriately step by step. Then accurately weigh

1.0 g (accurate to 0.0001

g) of the diluted and mixed specimen into a glass test tube (6.5), so that the concentration of chloropropanol in the weighed specimen is within the range of the standard working solution. If the chloropropanol content of the papermaking wet strength agent sample is low, it is possible to directly weigh

1.0 g (accurate to 0.0001

7.3 Test procedure

7.3.1 Extraction: Add 15 mL of sodium chloride solution (20%) (5.6) AND 20 μL of chloropropanol internal standard mixed standard intermediate solution (10 mg/L) (7.1.5) into the test tube containing the sample. After thorough mixing, use an ultrasonic cleaner (6.3) to extract at 40 °C for 30 min, to obtain the extraction solution. During the ultrasonic extraction process, the test tube mouth should be kept sealed until purification.

Note: If the sample contains water-absorbing resin, increase the volume of sodium chloride solution (20%) appropriately.

7.3.2 Purification: Weigh the macroporous diatomite (5.7) whose mass is equivalent to half the mass of the extraction solution (7.3.1); load it into a chromatographic column (5.8). Pour the extraction solution (7.3.1) into the diatomite chromatographic column and balance for 10 min. Use 10 mL of n-hexane (5.2) to rinse and discard the rinsing solution. Then use 18 mL of ethyl acetate (5.3) to elute; collect the eluent in a test tube. Add 3 g of anhydrous sodium sulfate (5.4) into the test tube; after letting it stand for 10 min, transfer the eluent (discard the anhydrous sodium sulfate part) to another clean stoppered test tube. Concentrate the eluent to nearly dryness by blowing nitrogen; add 2 mL of n-hexane (5.2) to reconstitute; wait for derivatization.

Note: The volume of the eluent after concentration by nitrogen blowing is approximately

0.5 mL.