

ICS 59.080.01

CCS W04



**NATIONAL STANDARD OF THE
PEOPLE'S REPUBLIC OF CHINA**

GB/T 42696-2023

Textiles - Determination of phosphate compounds

纺织品 磷酸酯类化合物的测定

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1 Scope

GB/T 42696-2023 gives the method for measuring organophosphate compounds in textiles. They are used mainly as flame retardants and plasticisers, and they became widespread precisely because they replaced the brominated flame retardants that were restricted before them. Several have since attracted their own concern - some are suspected carcinogens, others neurotoxic or endocrine active - and because they are not chemically bound to the fibre they migrate out of the textile over its life, into house dust and onto skin. They appear on restricted substance lists for children's products and for textiles in contact with skin, and enforcement requires a method. This document describes gas chromatography and gas chromatography-mass spectrometry methods for determining the content of eight phosphate compounds in textiles - GC for routine screening, GC-MS where confirmation of identity is required. It applies to all types of textiles. Under ICS 59.080.01 and CCS W04, it is written for textile testing laboratories, for brands and retailers running restricted substance programmes, and for the manufacturers of flame retardant and coated textiles who must demonstrate what their products contain.

This document describes the gas chromatography and gas chromatography-mass spectrometry methods for the determination of the content of 8 phosphate compounds in textiles. This document applies to all types of textiles.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

4 Principle

Use ethyl acetate to ultrasonically extract the specimen. After the extract is filtered through a filter membrane, use a gas chromatograph equipped with a flame photometric detector (P type) to measure; or use a gas chromatograph-mass spectrometer to measure. Use the external standard method for quantification.

5 Reagents and materials

Unless otherwise specified, all reagents used are chromatographically pure.

5.1 Tributyl phosphate (TBP): CAS number 126-73-8 (purity $\geq$ 98.5%).

5.2 Triphenyl phosphate (TPP): CAS number 115-86-6 (purity $\geq$ 99.7%).

5.3 Tri-o-cresyl phosphate (ToCP): CAS number 78-30-8 (purity $\geq$ 96%).

5.4 Tri-m-cresyl phosphate (TmCP): CAS number 563-04-2 (purity $\geq$ 95%).

5.5 Tri-p-cresyl phosphate (TpCP): CAS number 78-32-0 (purity $\geq$ 98%).

5.6 Trioctyl phosphate (TOP): CAS number 78-42-2 (purity $\geq$ 98%).

5.7 Diphenyl octyl phosphate (DPOP): CAS number 1241-94-7 (purity $\geq$ 90%).

5.8 Cresyl diphenyl phosphate (CDP): CAS number 26444-49-5 (purity $\geq$ 93%).

5.9 Ethyl acetate.

5.10 Standard stock solution: Use ethyl acetate (5.9) to prepare the standard substances listed in 5.1~

5.8 into a single-component standard stock solution with a mass concentration of approximately 1000 mg/L, respectively.

Note: The standard stock solution is stored in the dark at 0 °C~4 °C and is valid for 6 months.

5.11 Standard working solution: Pipette 8 appropriate amounts of phosphate compound standard stock solutions (5.10) respectively; place them in the same volumetric flask. Use ethyl acetate (5.9) to prepare a mixed standard working solution with a mass concentration of approximately 100 mg/L. Then according to work needs, use ethyl acetate (5.9) to prepare a standard working solution of appropriate concentration.

6 Apparatus

6.1 Gas chromatograph (GC-FPD): It is equipped with flame photometric detector (P type).

6.2 Gas chromatograph-mass spectrometer (GC-MS): It is equipped with electron impact ionization source (EI).

6.3 Ultrasonic generator: Working frequency is (40 ± 5) kHz.

6.4 Analytical balance: Graduation values are

0.1 mg and

0.01 g, respectively.

6.5 Vortex mixer.

6.6 Extraction tube: It has an airtight stopper; is about 50 mL; made of hard glass.

6.7 Disposable syringe.

6.8 Organic-phase needle filter head: Pore size is $0.45 \mu\text{m}$. retention times of the specimen solution and the standard working solution, perform qualitative analysis. Use the chromatographic peak area of the standard substance as the ordinate; use the concentration of the standard working solution as the abscissa; draw a standard working curve. Use the external standard method to perform quantitative analysis.

Note: When the above analysis conditions are used, the GC-FPD (P type) analysis chromatogram of 8 phosphate compound standard substances are shown in Appendix A. Cresyl diphenyl phosphate (CDP I) and cresyl diphenyl phosphate (CDP II) are isomers of each other; the CDP result is the sum of the isomers.

7.4 Gas chromatography-mass spectrometry analysis method

7.4.1 Gas chromatography-mass spectrometry analysis conditions Since the test results are related to the instrument and conditions used, it is impossible to give universal parameters for instrument analysis. The following parameters have been proven to be suitable for the test.

a) Chromatographic column: HP-5MS, 30 m x

0.25 mm x 0.25 μm ; or equivalent.

b) Column temperature programming:

c) Inlet temperature: 250 °C.

d) Mass spectrometer interface temperature is 250 °C.

e) Ion source temperature: 230 °C.

- f) Quadrupole temperature is 150 °C.
- g) Ionization method: EI.
- h) Ionization energy: 70 eV.
- i) Detection method: Selected ion monitoring (SIM) mode; the monitoring ions are shown in Table 1.
- j) Solvent delay: 8 min.
- k) Carrier gas: Helium; purity $\geq 99.999\%$; 1 mL/min.
- l) Injection method: Splitless injection; open the valve after 2 min.

8 Calculation and presentation of results

According to formula (1), calculate the content of each phosphate compound in the specimen. The test results are expressed as the content of each phosphate compound, respectively. Calculation results are expressed to one decimal place. Where: X_i - The content of phosphate compound i in the specimen, in milligrams per kilogram (mg/kg); C_i - The mass concentration of the phosphate compound i to be measured in the sample solution obtained from the standard working curve, in milligrams per liter (mg/L); C_{i0} - The mass concentration of phosphate compound i in the blank specimen solution in the sample solution obtained from the standard working curve, in milligrams per liter (mg/L); V - The final constant volume of sample solution, in milliliters (mL); m - Specimen mass, in grams (g); f - Dilution factor.

9 Limit of quantification and precision

9.1 Limit of quantification The limits of quantification of the 8 phosphate compounds in textiles using the gas chromatography method are all

2.0 mg/kg. The limits of quantification of the 8 phosphate compounds in textiles using gas chromatography-mass spectrometry are all