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NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

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Determination of key chemicals in consumer products - Part 1: Short chain chlorinated paraffins

消费品中重点化学物质检测方法 第1部分:短链氯化石蜡

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0 Place in the series

GB/T 44165 supplies test methods for the chemicals dealt with in GB/T 39498, the guide on controlling the use of key chemicals in consumer products. It is planned in nine parts, of which the first six have been published: short chain chlorinated paraffins, styrene migration, chloroethanes, 1,4-dichlorobenzene, phenol and acrylamide. The three still to come are polychlorinated naphthalenes, perfluorooctane sulfonate and perfluorooctanoic acid, and hexabromocyclododecane.

The document opens with a warning that those using it should have practical experience of regular laboratory work, that it does not point out every safety problem that may arise, and that the user is responsible for taking suitable safety and health measures and for meeting the conditions laid down in national regulations.

3 Terms and definitions

Short chain chlorinated paraffins, abbreviated SCCPs, are defined as the mixture of chloroalkanes having ten to thirteen carbon atoms, with the general formula

CmH2m+2-nCln where m runs from 10 to 13, CAS number 85535-84-8.

4 Principle

The prepared sample is extracted with n-hexane under ultrasound at room temperature. The extract is cleaned up with concentrated sulfuric acid and then measured on a gas chromatograph coupled to a mass spectrometer through a negative chemical ionisation source, quantification being by internal standard.

5 Reagents and materials

Unless stated otherwise the reagents are of analytical grade or better. n-Hexane is of chromatographic grade. Concentrated sulfuric acid is at a mass fraction of 98 per cent and the methane has a purity of at least 99.999 per cent.

Three reference materials are used, short chain chlorinated paraffins of 51.5 per cent, 55.5 per cent and 63 per cent chlorine content, each at a mass concentration of 100 mg per litre.

The internal standard is epsilon-hexachlorocyclohexane, CAS number 6108-10-7, or 1,1,1,3,10,11-hexachloroundecane, CAS number 601523-28-8, or another suitable substance. A stock solution of it is made up in n-hexane at 100 mg per litre.

6 Apparatus

A gas chromatograph and mass spectrometer fitted with an electron capture negative chemical ionisation source; an analytical balance reading to 0.1 mg; an ultrasonic extractor of 250 W at 53 kHz or equivalent; a grinder, scissors or other suitable crushing equipment; a centrifuge running at not less than 10000 revolutions per minute; stoppered glass bottles of 25 mL; stoppered colorimetric tubes of 10 mL; and organic phase membrane filters of 0.22 μm pore size.

7 Sample pretreatment

A solid sample is crushed at room temperature to particles under 2 mm by 2 mm by 2 mm. A liquid sample is simply stirred even with a glass rod.

For a solid test portion, 0.5 g weighed to 0.1 mg goes into a 25 mL stoppered glass bottle with 10.0 mL of n-hexane and is sonicated at room temperature for 60 +/- 2 min, then cooled to room temperature. For a liquid test portion, 0.5 g weighed to 0.1 mg goes into a 10 mL stoppered colorimetric tube, is mixed with n-hexane and made up to the mark, sonicated for the same time, cooled, transferred to a centrifuge tube and spun for 10 min, the supernatant being taken.

For cleanup, 5 mL of the extract is measured into a glass tube with 5 mL of concentrated sulfuric acid, vortexed and separated in the centrifuge, and the upper organic layer is

collected. This is repeated until the lower acid layer runs clear or white, not more than five times in all. The cleaned extract is passed through the membrane filter.

Finally 1 mL of the cleaned extract is measured into a vial and 5 µL of the internal standard stock solution is added. The amount added may be adjusted to suit the response of the internal standard, so long as it matches the internal standard content of the calibration solutions.

8 Determination

Because the result depends on the instrument used, no general set of parameters can be given; the parameters chosen have to separate the analyte from the other components, and the following set has been shown to work. The column is 30 m long with an internal diameter of 0.25 mm and a stationary phase of 5 per cent phenyl and 95 per cent dimethylpolysiloxane, in fused silica, or an equivalent. The injector is at 280 degrees Celsius, injection is splitless, and the oven is held at 100 degrees Celsius for 1 min, raised at 50 degrees Celsius per minute to 300 degrees Celsius and held there 9 min. The transfer line is at 300 degrees Celsius. The carrier gas is helium of at least 99.999 per cent purity at 1.0 mL per minute. The ion source is at 160 degrees Celsius, with a note that the effect of source temperature on fragment formation should be understood before the optimum is fixed. Methane is the reagent gas at 1.5 mL per minute, ionisation is negative chemical, acquisition is in selected ion mode and the solvent delay is 3.0 min. The film thickness and the injection volume are printed with their micro prefix lost in the source file, so those two figures are not repeated here.

The ion table covers 24 congener groups, from the five chlorine to the ten chlorine members of each carbon number from ten to thirteen, and fixes one quantifier and one qualifier ion for each. For the ten carbon series the quantifier and qualifier masses are 277 and 279, 313 and 315, 347 and 349, 381 and 383, 415 and 417, and 449 and 451. Across the whole table the quantifier masses run from 277 to 493.

Identification is by comparing the chromatographic peaks of the characteristic ions and their retention times between the calibration solution and the test solution, with reference to the chromatograms of Annex A.

The calibration solutions are made up in n-hexane from the three reference materials, all at a mass concentration of 50 mg per litre and differing only in chlorine content, which is set at 53.5, 55.5, 56.25, 57.75 and 59.25 per cent. The volume ratios that give these are five parts of the 51.5 per cent material with five parts of the 55.5 per cent; ten parts of the 55.5 per cent alone; then nine, seven and five parts of the 55.5 per cent with one, three and five parts of the 63 per cent material. One millilitre of each goes into a vial with 5 µL of the internal standard stock, the amount again adjustable to the response.

These volume ratios are given as an example. In practice the calibration solutions should be

made up close in concentration to the sample, and at least five different chlorine contents should be covered; where the sample is far from the calibration range it should be diluted into it before quantification. Where the sample also holds medium chain chlorinated paraffins the target peak may tail, and the integration of the sample peak is then cut off at the point where the corresponding peak of the calibration solution ends.

Quantification does not rest on a single calibration line. For each calibration solution the total relative peak area of the 24 congener groups is worked out against the internal standard peak; from it an overall response factor is obtained by dividing by the mass concentration and the injection volume of the standard; and a measured chlorine content is obtained by weighting the theoretical chlorine content of each congener group by its share of the total relative peak area. A straight line is then fitted between overall response factor and measured chlorine content, and it is that line which serves to quantify the sample.

9 Calculation of results and limit of quantification

The content of short chain chlorinated paraffins in the sample follows from the total relative peak area of the sample and its make-up volume, divided by the overall response factor of the sample, the injection volume and the mass of the test portion; it is given in milligrams per kilogram and reported to three significant figures.

The limit of quantification of the method is 100 mg per kilogram.

B Annex B, theoretical chlorine content

An informative annex tabulates, for each of the 24 congener groups, the relative molecular mass and the theoretical chlorine content, the latter being the number of chlorine atoms times the relative atomic mass of chlorine divided by the relative molecular mass of the group.

Relative molecular masses run from 314.5 for the five chlorine, ten carbon member to 529.0 for the ten chlorine, thirteen carbon member. Theoretical chlorine contents run from 0.50 to 0.73, rising with the number of chlorine atoms and falling with the number of carbon atoms.

C Annex C, results of the interlaboratory trial

Four representative real samples were circulated to seven laboratories and the results treated to GB/T 6379.1 and GB/T 6379.2. No laboratory was rejected as an outlier in any of the four.

For the PVC plastic sample the mean content was 18618 mg per kilogram, with a repeatability standard deviation of 591 mg per kilogram, a repeatability coefficient of variation of 3.17 per cent and a repeatability limit of 1654 mg per kilogram; the