The People's Republic of China

EDICT OF GOVERNMENT

In order to promote public education and public safety, equal justice for all, a better informed citizenry, the rule of law, world trade and world peace, this legal document is hereby made available on a noncommercial basis, as it is the right of all humans to know and speak the laws that govern them.

GB 18581 (2008) (English): Indoor decorating and refurbishing materials – limit of harmful substances of solvent coatings for woodenware

BLANK PAGE

ICS 87.040
G 51

National Standard of the People's Republic of China

GB18581-XXXX
Replaces GB 18581-2001

Indoor decorating and refurbishing materials – limit of harmful substances of solvent coatings for woodenware

Draft for approval

Issue Date: XXXX – XX – XX

Implementation Date: XXXX – XX – XX

Issued by the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China

Standardisation Administration of the People's Republic of China (SAC)

Foreword

This Standard replaces GB 18581-2001, "Indoor decorating and refurbishing materials – limit of harmful substances of solvent coatings for woodenware".

The main technical differences between this Standard when compared to GB 18581-2001 are:

- the applicable range of this Standard are polyurethane-based, nitrocellulose-based, alkyd-based solvent coatings (including top coats and base coats) and all types of solvent-based putties for woodenware used for indoor and factory decorating and refurbishing;
- the addition of all types of solvent-based putties in the applicable range and their prescribed harmful substances limit;
- the clarified applicable range does not apply to irradiation curable coatings;
- the addition of the content limit requirement of methanol in nitrocellulose coatings;
- the total limit requirement of methylbenzene and xylene clearly clarified as the total limit requirement of methylbenzene, xylene and ethylene;
- the alteration of the content limit requirement of free diisocyanate to the total content limit requirement of free diisocyanate (TDI + HDI);
- the addition of the content limit requirement of halohydrocarbon;
- in all types of coatings, the limit values of total of the volatile organic compound (VOC), benzene, methylbenzene, xylene, and ethylbenzene, as well as free diisocyanate (TDI+HDI) are more strictly limited;
- the addition of the definition of volatile organic compound (VOC) and its content, specified the corresponding test method;
- specification of the test methods for methanol and halo-hydrocarbon;
- the modification and perfection of the test method for total of benzene, methylbenzene, ethylbenzene and xylene;
- the test method for soluble heavy metals has been modified and perfected.

Appendix A, Appendix B, and Appendix C to this Standard are normative annexes.

This Standard is proposed by the China Petroleum and Chemical Industry Association (CPCIA)

This Standard is under the jurisdiction of the National Technical Committee of Paint & Pigments for Standardisation

The organisation responsible for drafting this Standard:

The organisations that participated in the drafting of this Standard:

The main drafters of this Standard:

This Standard was first issued on 10 December 2001. This is the first revision of this Standard.

The National Technical Committee of Paint & Pigments for Standardisation is entrusted for the interpretation of this Standard.

Indoor decorating and refurbishing materials –
limit of harmful substances of solvent coatings for woodenware

1 Scope

This Standard specifies the allowable limit requirements, the test methods, inspection rules, packaging symbols, painting safety and protection methods of substances which are harmful to human health and the environment contained in polyurethane based, nitrocellulose based and alkyd-based solvent coatings and all types of solvent-based putties for indoor decorating and refurbishing.

This Standard applies to polyurethane based, nitrocellulose based and alkyd-based solvent coatings, as well as all types of solvent-based putties for indoor and factory woodenware decorating and refurbishing. This Standard does not apply to irradiation curable coating.

2 Normative References

The provisions of the following documents become provisions of this Standard after being referenced. For dated reference documents, all later amendments (excluding corrigenda) and versions do not apply to this Standard; however, the parties to the agreement are encouraged to study whether the latest versions of these documents are applicable. For undated reference documents, the latest versions apply to this Standard.

GB/T601 Chemical reagent – Preparations of standard volumetric solutions

GB/T1250 Expression methods and determination methods for limit values

GB/T1725 Paints, varnishes and plastics – Determination of non-volatile matter content (GB/T 1725-2007, ISO 3251:2003, IDT)

GB/T3186 Paints, varnishes and raw materials for paints and varnishes – Sampling (GB/T 3186-2006, ISO 15528:2000, IDT)

GB/T6682 Water for analytical laboratory use – Specification and test methods (GB/T6682-1992 neq ISO3696:1987)

GB/T6750 Paints and varnishes – Determination of density – Part 1: Pyknometer method (GB/T6750-2007, ISO 2811-1:1997, IDT)

GB/T9750 Marks for package of coating products

GB/T9754 Paints and varnishes – Measurement of specular gloss of non-metallic paint films at 20^{o}, 60^{o} and 85^{o}

GB/T18446 Binders for paints and varnishes – Determination of monomeric diisocyanates in polyisocyanate resins

GB18582 Indoor decorating and refurbishing materials – Limit of harmful substances of paints for interior wall

3 Terms and definitions

The terms and definitions listed below apply to this Standard.

3.1 Volatile organic compound (VOC)

Any organic compound which, under the standard pressure of 101.3Kpa, has an initial boiling point equal to or below 250^{o}C, shall be considered a volatile organic compound.

3.2 Volatile organic compound content

The content value of volatile organic compounds measured in accordance with prescribed test methods to test the product.

> Note 1: the content value of volatile organic compound for all types of coatings and all types of putties shall be represented by gram per litre (g/L).

3.3 Polyurethane coatings

Type of coating with polyurethane resin as the main film forming matter, where the polyurethane resin is generated by the reactions between polyisocyanate and the compound contains active hydrogen.

3.4 Nitrocellulose coatings

Type of coating with cellulose nitrate as the main film forming matter, where the cellulose nitrate is generated by the reactions between cellulose esterification and the mixture of nitric acid and sulphuric acid.

3.5 Alkyd coatings

Type of coating with alkyd resin as the main film forming matter, where the alkyd resin is prepared by the polycondensation of polybasic acid, fatty acid (or vegetable oil) and polyols.

4 Requirements

The limit of the harmful substances contained in products must conform to the requirements set out in Table 1:

Table 1 Limit requirements of harmful substances

Item	Limit Value				
	Polyurethane coatings		Nitrocellulose coatings	Alkyd coatings	Putty
	Top coat	Base coat			
Volatile organic compounds (VOC)[a]	Gloss (60^{o}) ≥ 80, ≤580 (g/L) Gloss (60^{o}) < 80, ≤670 (g/L)	≤ 670 (g/L)	≤ 720 (g/L)	≤ 500 (g/L)	≤ 550 (g/L)
Benzene	≤ 0.3				

(Total of Methylbenzene, Xylene and Ethylbenzene)[a]/%		≤ 30	≤ 30	≤ 5	≤ 30
Total free diisocyanate (TDI+HDI)[b]/%		≤ 0.4	-	-	-
Methanol[a]/%		-	≤ 0.3	-	≤ 0.3 (limited to nitrocellulose putty)
Halohydrocarbon [a,c]/%		≤ 0.1			
Heavy metal (limited to coloured paint and putty)/(mg/kg)	Soluble lead	≤ 90			
	Soluble cadmium	≤ 75			
	Soluble chromium	≤ 60			
	Soluble mercury	≤ 60			

a *shall be determined after being blended in accordance with the specified proportions and the dilution rate of the product. If the amount of the dilution solvents used is within a certain range, the total shall be determined after being diluted in accordance with the recommended maximum dilution quantity*.
b *if polyurethane coatings specified the dilution rate or when formed by two components or multi components, the content of firming agents (contain free diisocyanate prepolymer) shall be determined first, then the contents in the blended coating shall be calculated in accordance with the specified proportion of the product. If the amount of dilution solvent used is within a certain range, the contents shall be determined in accordance with the recommended minimum dilution quantity.*
c *including dichloromethane, dichloroethane (1,1- dichloroethane, 1,2 dichloroethane), trichloromethane (1,1,1 trichloromethane , 1,1,2 trichloromethane), trichloroethane, carbon tetrachloride*.

5 Test methods

5.1 Sampling

Product sampling shall be performed in accordance with the provisions specified in GB/T3186.

5.2 Test methods

5.2.1 The volatile organic compounds (VOC) test shall be performed in accordance with the provisions set out in Appendix A to this Standard.

5.2.2 The methanol, benzene, methylbenzene, ethylbenzene and xylene tests shall be performed in accordance with the provisions set out in Appendix B to this Standard.

5.2.3 The content test of free diisocyanate (TDI+HDI) shall be conducted in accordance with the provisions specified in GB/T18446-XXXX.

5.2.4 The content test of halohydrocarbon shall be conducted in accordance with the provisions specified in Appendix C.

5.2.5 The content test of soluble heavy metals (lead, cadmium, chromium and mercury) shall be conducted in accordance with the provisions specified in GB 18582.

6 Inspection rules

6.1 The entire requirements listed in this Standard are inspection items for type approval.

6.1.1 Under normal production conditions, the inspection for type approval shall be conducted at least once per year.

6.1.2 Under any of the following conditions, the inspection for type approval shall be conducted at any time:

- first finalisation of a newly designed product;
- if the place of production of the product is changed;
- if major changes are made to the dispensation formula, technology, the main source of raw materials and the product construction proportion;
- if production is stopped for three months then re-started again.

6.2 Determination of inspection results

6.2.1 The determination of the inspection results shall be conducted in accordance with the comparison method using round off values as specified in GB/T1250.

6.2.2 The inspection result statement shall clearly indicate the proportions of the components.

6.2.3 When the inspection results of all items have met the requirements of this Standard, then the product can be considered as in conformance with this Standard.

7 Packaging symbols

7.1 In addition to complying with the provisions specified in GB/T9750, the product packaging symbol must also clearly state that the product meets the inspection qualifications of this Standard.

7.2 For coatings which are set-formed by two components or multi-components, the proportion of each component must be clearly indicated on the packaging symbol. For coatings which need to be diluted when carrying out construction, the dilution proportion must be indicated on the packaging symbol.

8 Painting safety and protection

8.1 The room must be well ventilated when painting.

8.2 Construction personnel must wear the necessary protective clothing when painting.

8.3 Interior ventilation must be continuously maintained after painting is completed.

Appendix A

(Normative Annex)

Content Determination of Volatile Organic Compound (VOC)

A.1 Theory

The sample shall be tested using the gas chromatography method. If any organic compound with a boiling point greater than 250^{o} C is not detected in the sample, then the tested volatile value shall be the VOC content of the product; if any organic compound with a boiling point greater than 250^{o}C is detected in the sample, then the qualitative determination and quantitative analysis shall be conducted on the detected organic compound in the sample which has a boiling point greater than 250^{o}C. The difference value in deducting the compound content (V_{paint}) with a boiling point greater than 250^{o}C from the volatile (V) shall be the VOC content of the product.

A.2 Materials and reagents

A.2.1 Carrier gas: nitrogen, purity must be at least 99.995%;

A.2.2 Combustion gas: hydrogen, purity must be at least 99.995%;

A.2.3 Combustion-supporting gas: air;

A.2.4 Assisting gas (septum purge and make-up gas): nitrogen which has the same properties as the carrier gas;

A.2.5 Internal standard: the compound which is not contained in the sample, which can be completely separated from other components on the chromatogram. The purity of the internal standard must be at least 99% (mass fraction) or a prescribed purity. For example: dimethyl phthalate, diethyl phthalate etc.

A.2.6 Calibration compound: The compound used for correction must be at least 99% (mass fraction) or a prescribed purity.

A.2.7 Dilution solvent: the organic solvent used for diluting the sample must not contain any substances that are able to influence the tests. The purity of the dilution solvent must be at least 99% (mass fraction) or a prescribed purity.

A.2.8 Marker: the compound used to divide the VOC component and non-VOC component in accordance with the VOC definition. In this Standard, the marker is specified as diethyl adipate (boiling point is 251^{o}C).

A.3 Instruments and facilities

A.3.1 Gas chromatograph, equipped with the following devices

A.3.1.1 Sample injection port of the split injector, the liner of the vaporisation chamber is replaceable;

A.3.1.2 Programmed temperature controller;

A.3.1.3 Detector;

Any one of the three detectors listed below can be selected:

A.3.1.3.1 Flame Ionisation Detector (FID);

A.3.1.3.2 A corrected and tuned mass spectroscopy or any other mass selective detector;

A.3.1.3.3 A corrected Fourier Transform Infrared Spectrometer (FT-IR optical spectrometer).

Note: if any of the detectors mentioned in A.3.1.3.2 and A.3.1.3.3 are selected to conduct the qualitative determination of the organic compounds with a boiling point greater than 250°C, then the detector must be connected to the gas chromatograph and operated in accordance with the relevant instructions specified by the detector manufacturer.

A.3.1.4 Chromatography column: polydimethylsiloxane capillary column;

A.3.2 Sample Injection Device: microinjector, 10μl;

A.3.3 Sample Preparation Bottle: a glass bottle with a capacity of appropriately 10ml, air-tight lid;

A.3.4 Scales: precision to 0.1mg.

A.4 Test conditions of gas chromatography

Chromatographic column: polydimethylsiloxane capillary column, 30m x 0.25mm x 0.25μm or other equivalent types;

Temperature of the sample injection port: 300°C;

Detector: FID, temperature: 300°C;

Column temperature: the initial temperature must be 160°C and maintained for 1 minute; the temperature is then increased by increments of 10°C per minute until it reaches 290°C, maintaining this temperature for 15 minutes;

Flow rate of the carrier gas: 1.2ml per minute;

Split ratio: sample split-injected, adjustable split ratio;

Sample size: 1.0μl

Note: the test conditions of the gas chromatography can be selected on the basis of the characteristics of the devices used and the actual conditions of the test sample.

A.5 Test procedures

A.5.1 Density

Mix together all the prescribed sample components in accordance with the proportion rate specified in the product instructions, stir until well mixed, and then determine the density (ρ*)* of the sample in accordance with the provisions specified in GB/T 6750. The test temperature must be 23± 2°C.

A.5.2 The gloss measurement of the polyurethane coatings must be conducted in accordance with the provisions specified in GB/T9754. After mixing the main agent, the firming agent and the dilution solvent together in accordance with the proportion rate specified in the product instructions, use a wet film applicator with a slot depth of (100± 2)μm to produce a sample board. After the sample board is dry, use a specular gloss meter of 60° to obtain measurements.

A.5.3 Volatile matter (V)

Mix all the prescribed sample components in accordance with the proportion rate specified in the product instructions, stir until well mixed, then determine the volatile matter(V) content of the sample in accordance with the provisions specified in GB/T 1725. Test conditions shall be (105± 2)°C/3h.

A.5.4 Volatile Organic Compound (VOC)

A.5.4.1 The determination of the VOC content when the sample does not contain organic compounds with a boiling point greater than 250°C.

If, after the qualitative analysis specified in A.5.4.2.2, no organic compound with a boiling point greater than 250°C is detected in the sample, then the VOC content in the sample shall be

determined by formula (A.1).

$$VOC = V \times \rho \times 1000 \cdots\cdots (A.1)$$

Where:

VOC – the VOC content in the sample. Unit of measurement is grams per litre (g/L);

V – the mass fraction of the volatile matter in the sample;

ρ – the density of the sample when the temperature is (23± 2)^{o}C. Unit of measurement is grams per millilitre (g/ml);

1000 – the conversion factor.

A.5.4.2 The determination of the VOC content when the sample containing organic compound which has a boiling point greater than 250^{o}C

A.5.4.2.1 Optimisation of chromatographic parameters

According to the test conditions of chromatography specified in A.4, prescribed calibration compounds must be used to carry out optimised treatment, in order to maintain the optimum accuracy, stability and separation efficiency of the device.

A.5.4.2.2. Qualitative analysis

Inject the marker into the gas chromatograph and measure its retention time on the polydimethylsiloxane capillary column in order to determine the integral starting point on the chromatogram in accordance with the VOC definition specified in 3.1.

Mix the prescribed sample components in accordance with the proportion rate specified in the product instructions, stir until well mixed, then inject the sample into the gas chromatograph, record the chromatogram, and carry out qualitative determination for each compound with a retention time longer than the marker. The preferred selective method is to jointly use gas chromatography, the mass selective detector (A.3.1.3.2) or the FT-IR infrared optical spectrometer (A.3.1.3.3), and to use the test conditions of gas chromatography specified in A.4.

A.5.4.2.3 Calibration

A.5.4.2.3.1 If the compound suitable for calibration is available for purchase, then the relative correction factor shall be determined by the following methods.

A.5.4.2.3.1.1 Preparation of the calibration sample: weigh out a certain amount (precise to 0.1mg) of each calibration compound approved in A.5.4.2.2 and place into the sample preparation bottle (A.3.3). The weighted mass and the content of each compound in the test sample shall be of the same order of magnitude. Then weigh out the internal standard (A.2.5) which has the same mass as the test compounds, and put into the same sample preparation bottle, use an appropriate dilution solvent (A.2.7) to dilute the mixture, seal up the bottle and shake until the dilution is well mixed.

A.5.4.2.3.1.2 Determination of the relative correction factor: under the same test conditions of gas chromatography of the test sample, optimisation of the chromatographic parameters in accordance with A.5.4.2.1. Inject a suitable amount of calibration compound into the gas chromatograph and record the chromatogram. The relative correction factor of each compound shall be determined by formula (A.2) respectively:

$$R_i = \frac{m_{ci} \times A_{is}}{m_{is} \times A_{ci}} \quad \text{(A.2)}$$

Where:

R_i – the relative correction factor of the compound i;

m_{ci} – the mass of the compound in the calibration mixture. Unit of measurement is grams (g);

m_{is} – the mass of the internal standard in the calibration mixture. Unit of measurement is grams (g);

A_{is} – the peak area of the internal standard;

A_{ci} – the peak area of the compound i.

Parallel test twice, take the mean value of the two test results as the R_i value. Its relative deviation must be less than 5%; retain three significant numbers.

A.5.4.2.3.2 In the case of a chromatographic peak which fails the qualitative determination, or the organic compound used for calibration failed the commercialisation, then the relative correction factor is assumed to be 1.0.

A.5.4.2.4 Sample tests

A.5.4.2.4.1 Sample preparation: according to the product instructions, blend all prescribed sample components; stir until the mixture is well mixed. Weigh out 2g (precise to 0.1mg) of the well blended mixture, and weigh out the internal standard (A.2.5) which has the same mass as the test sample, put them into the sample preparation bottle (A.3.3), add a suitable amount of dilution solvent (A.2.7) (use injectable sample) into the same bottle to dilute the sample, seal the bottle and shake until the dilution is well mixed.

A.5.4.2.4.2 According to the optimisation conditions during calibration time to set the device parameters.

A.5.4.2.4.3 Inject the marker (A.2.8) into the gas chromatograph and record its retention time on the polydimethylsiloxane capillary column in order to determine the integral starting point on the chromatogram in accordance with the VOC definition specified in 3.1.

A.5.4.2.4.4 Inject the 1.0µl sample prepared in A.5.4.2.4.1 into the gas chromatograph, record the chromatogram, and record the peak area of every compound with a retention time longer than the marker, then determine the mass fraction of each compound where its boiling point is greater than 250°C respectively.

$$V_{painti} = \frac{m_{is} \times A_i \times R_i}{m_s \times A_{is}} \quad \text{(A.3)}$$

Where:

$V_{paint\ i}$ – the mass fraction of compound i which is contained in the sample and its boiling point is greater than 250°C. Unit of measurement is gram per gram (g/g);

R_i – the relative correction factor of compound i;

m_{is} – the mass of the internal standard. Unit of measurement is grams (g);

m_s – the mass of the sample. Unit of measurement is grams (g);

A_i – the peak area of compound i;

A_{is} – the peak area of the internal standard.

Parallel test twice, the mean value from the two test results shall be regarded as the $V_{paint\ i}$ value.

A.5.4.2.4.5 The content of the compound which is contained in the sample with a boiling point is greater than 250°C shall be determined by the formula (A.4).

$$V_{paint} = \sum_{i=1}^{n} V_{painti} \quad \text{.....(A.4)}$$

where:

V_{paint} – the mass fraction of the compound which is contained in the sample and has a boiling point is greater than 250°C.

A.5.4.2.5 The content of the compound which is contained in the sample and has a boiling point is equal to or less than 250°C, shall be determined by the formula (A.5).

$$VOC = \square V - V_{paint} \square \times \square \times 1000 \quad \text{.....(A.5)}$$

Where:

VOC - the content of the compound which is contained in the sample and its boiling point is equal or less than 250°C;

V – the mass fraction of the volatile matter which is contained in the sample;

V_{paint} – the mass fraction of the compound which is contained in the sample and has a boiling point is greater than 250°C.

ρ – the density of the sample when the temperature range is (23± 2)°C. Unit of measurement is grams per millilitre (g/ml);

1000 – the conversion factor.

A.6 Accuracy

A.6.1 Repeatability

Tests carried out by the same operator, in the same laboratory, using the same device, within a certain time interval, on the same sample should provide a relative deviation in the tested results of less than 5%.

A.6.2 Reproducibility

Tests carried out by different operators, in different laboratories, on the same sample should provide a relative deviation in the tested results of less than 10%.

Appendix B

(Normative Annex)

Content Determination of methanol, benzene, methylbenzene, ethylbenzene, and xylene

B.1 Theory

After the sample is diluted, inject the dilution directly into the gas chromatograph. After separation by the chromatographic column, test the sample with a hydrogen flame ionisation detector. Use the internal standard method to determine the amount of the contents.

B.2 Materials and reagents

B.2.1 Carrier gas: nitrogen, purity must be at least 99.995%;

B.2.2 Combustion gas: hydrogen, purity must be at least 99.995%;

B.2.3 Combustion-supporting gas: air;

B.2.4 Assisting gas (septum purge and make-up gas): nitrogen with the same properties as the carrier gas;

B.2.5 Internal standard: the compound which is not contained in the sample, which can be completely separated from other components on the chromatogram. The purity of the internal standard must be at least 99% (mass fraction) or a prescribed purity. For example: n-heptane, and n-pentane etc,.

B.2.6 Calibration compound: methanol, benzene, methylbenzene, ethylbenzene and xylene, their purity must be at least 99% (mass fraction) or a prescribed purity.

B.2.7 Dilution solvent: the organic solvent used for diluting the sample, must not contain any substances that are able to influence the tests. The purity of the dilution solvent must be at least 99% (mass fraction) or a prescribed purity. For example: ethyl acetate, n-hexane etc.

B.3 Instruments and facilities

B.3.1 Gas chromatograph, equipped with the following devices

B.3.1.1 Sample injection port of the split injector, the liner of the vaporisation chamber is replaceable;

B.3.1.2 Programmed temperature controller;

B.3.1.3 Detector: Flame Ionisation Detector (FID);

B.3.1.4 Chromatographic column: must enable the test substances to be completely separated from other components, such as a polydimethylsiloxane capillary column, 6% cyano-propylphenyl /94% polydimethylsiloxane capillary column, polyethylene glycol capillary column or other equivalent types;

B.3.2 Sample Injection Device: microinjector, 10μl;

B.3.3 Sample Preparation Bottle: a glass bottle with a capacity of appropriately 10ml, air-tight lid;

B.3.4 Scales: precise to 0.1mg.

B.4 Test conditions of gas chromatography

Chromatographycolumn: polydimethylsiloxane capillary column, 30m x 0.25mm x 0.25μm or other equivalent types;

Temperature of the sample injection port: 240^{o}C;

Detector temperature: 280^{o}C;

Column temperature: the initial temperature must be 50^{o}C and maintained for 5 minutes, after which the temperature should be increased by increments of 10^{o}C per minute until it reaches 280^{o}C, maintaining this temperature for 15 minutes;

Pre-column pressure: 35kPa;

Split ratio: sample split-injected, adjustable split ratio;

Sample size: 1.0μl

Note: the test conditions of the gas chromatography can be selected on the basis of the characteristics of the devices used and the actual conditions of the test sample.

B.5 Test procedures

B.5.1 Optimisation of chromatographic parameters

According to the test conditions of chromatography specified in B.4, prescribed calibration compounds must be used to carry out optimised treatment, in order to maintain the optimum accuracy, stability and separation efficiency of the device.

B.5.2 Calibration

B.5.2.1 Preparation of the calibration sample: weigh out a certain amount (precise to 0.1mg) of each calibration compound approved in B.2.6 and place into the sample preparation bottle (B.3.3). The weighted mass and the content of each compound in the test sample must be of the same order of magnitude. Then weigh out the internal standard (B.2.5) which has the same mass as the test compounds, and put into the same sample preparation bottle. Use an appropriate dilution solvent (B.2.7) to dilute the mixture, seal up the bottle and shake until the dilution is well mixed.

B.5.2.2 Determination of the relative correction factor: under the same test conditions of gas chromatography of the test sample, optimisation of the chromatographic parameters in accordance with B.5.1. Inject a suitable amount of calibration compound into the gas chromatograph and record the chromatogram. The relative correction factor of each compound shall be determined by the formula (A.2) respectively:

$$R_i = \frac{m_{ci} \times A_{is}}{m_{is} \times A_{ci}} \quad \text{(B.1)}$$

Where:

R_i – the relative correction factor of methanol, benzene, methylbenzene, ethylbenene, and xylene respectively corresponding to the internal standard;

m_{ci} – the individual mass of methanol, benzene, methylbenzene, ethylbenene, and xylene in the calibration mixture. Unit of measurement is grams (g);

m_{is} – the mass of the internal standard in the calibration mixture. Unit of measurement is grams (g);

A_{is} – the peak area of the internal standard;

A_{ci} – the peak area of methanol, benzene, methylbenzene, ethylbenzene, and xylene in the calibration mixture.

Parallel test twice, take the mean value of the two test results as the R_i value. Its relative deviation must be less than 5%; retain three significant numbers.

B.5.3 Sample test

B.5.3.1 Sample preparation: according to the product instructions, blend all prescribed sample components, stir until the mixture is well mixed. Weigh out 2g (precise to 0.1mg) of the well blended mixture, and weigh out the internal standard (B.2.5) which has the same mass as the test sample, put them into the sample preparation bottle (B.3.3), add a suitable amount of dilution solvent (B.2.7) (use injectable sample) into the same bottle to dilute the sample, seal the bottle and shake the bottle until the dilution is well mixed.

B.5.3.2 According to the optimisation conditions during calibration time to set the device parameter.

B.5.3.3 Inject 1.0μl sample which is prepared in B.5.3.1 into the gas chromatograph, record the chromatogram, the content of the test substances (methanol, benzene, methylbenzene, ethylbenzene, and xylene) contained in the sample shall be determined by the formula (B.2).

$$m_I = \frac{m_{is} \times A_i \times R_i}{m_s \times A_{is}} \times 100 \quad \cdots\cdots (B.2)$$

Where:

m_I – the mass fraction of the test component i in the sample;

R_i – the relative correction factor of test component i;

m_{is} – the mass of the internal standard, unit of measurement is grams (g);

m_s – the mass of the sample, unit of measurement is grams (g);

A_i – the peak area of the test component i;

A_{is} – the peak area of the internal standard.

Note: in the case that test substances are not be able to separated effectively when under test conditions of gas chromatography specified in B.4, and therefore the determination can not be correctly deduced, then other types of chromatography columns (see the list in B.3.1.4) or other test conditions of gas chromatographs used for the replacement shall be permitted, to enable the test substances to be efficiently separated and the content determination can be deduced.

Parallel test twice, take the mean value of the two test results as the content of the test substance. Its relative deviation must be less than 5%.

B.6 Accuracy

B.6.1 Repeatability

Tests carried out by the same operator, in the same laboratory, using the same device, within a certain time interval, on the same sample should provide a relative deviation in the tested results of less than 5%.

B.6.2 Reproducibility

Tests carried out by different operators, in different laboratories, on the same sample should provide a relative deviation in the tested results of less than 10%.

Appendix C

(Normative Annex)

Content Determination of halohydrocarbon

C.1 Theory

After the sample is diluted with dilution solvent, inject the dilution directly into the gas chromatograph, after the dichloromethane, dichloroethane, trichloromethane, trichloroethane, and carbon tetrachloride are completely separated from other components by a capillary gas chromatography column; conduct the test with an electron capture detector. Use the internal standard method to determine the amount.

C.2 Materials and reagents

C.2.1 Carrier gas: nitrogen, purity must be at least 99.995%;

C.2.2 Assisting gas (septum purge and make-up gas): nitrogen with the same properties as the carrier gas;

C.2.3 Calibration compound: dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, trichloromethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane and carbon tetrachloride which are used for calibration, their purity must be at least 99% (mass fraction) or a prescribed purity;

C.2.4 Dilution solvent: the organic solvent used to dilute the sample, its purity must be at least 99% (mass fraction) or a prescribed purity. For example: ethyl acetate, n-hexane etc.

C.2.5 Internal Standard: the compound which is not contained in the sample that can be completely separated from other components of the chromatogram. Its purity must be at least 99% (mass fraction) or a prescribed purity. For example: bromopropane.

C.3 Instruments and devices

C.3.1 Gas chromatograph, equipped with the following devices:

C.3.1.1 Sample injection port of the split injector, the liner of the vaporisation chamber is replaceable;

C.3.1.2 Programmed temperature controller

C.3.1.3 Electron Capture Detector (ECD);

C.3.1.4 Chromatography Column: must enable the test components to be completely separated from other components, such as a (5% phenyl) 95% methyl polysiloxane capillary column or other equivalent types;

C.3.2 Sample Injection Device: 10μl microinjector;

C.3.3 Sample Preparation Bottle: a capacity of 10ml glass bottle, air-tight bottle lid;

C.3.4 Scales: precision 0.1mg.

C.4 Chromatographic analysis conditions

Chromatography column: hp-5: (5% phenyl) 95% methyl polysiloxane capillary column, 30m x 0.25mm x 0.25μm or other equivalent types;

Temperature of the sample injection port: 250°C;
Column temperature: the initial temperature must be 40°C and maintained for 15 minutes, then the temperature is increased by increments of 10°C per minute until it reaches 150°C, maintaining this temperature for 2 minutes; then the temperature is increased by increments of 50°C per minute until it reaches 250°C, maintaining this temperature for 2 minutes;
Temperature of the detector: 300°C;
Flow rate of the carrier gas: 2.0ml/minute;
Split ratio: sample split-injected, adjustable split ratio;

Note: In order to select the best test conditions of the gas chromatograph, the test conditions of the gas chromatography can be selected on the basis of the characteristics of the devices used and the actual conditions of the test sample.

C.5 Test procedures

C.5.1 Optimisation of chromatographic parameters

According to the test conditions of the chromatographic condition specified in C.4, prescribed calibration compounds must be used to carry out optimised treatment, in order to maintain the optimum accuracy, stability and separation efficiency of the device. The sample size and the split ratio must correspond to each other, to avoid exceeding the capacity of the chromatographic column, and be within the linear range of the device detector.

C.5.2 Determination of the retention time of the test substances

According to C.5.1 adjust the device to its best state, after the device is steady, inject into 1.0μl standard solution which contains all the test substances. Record the retention time of each test substance. See Figure 1 for the peak sequence and retention time of each test substance.

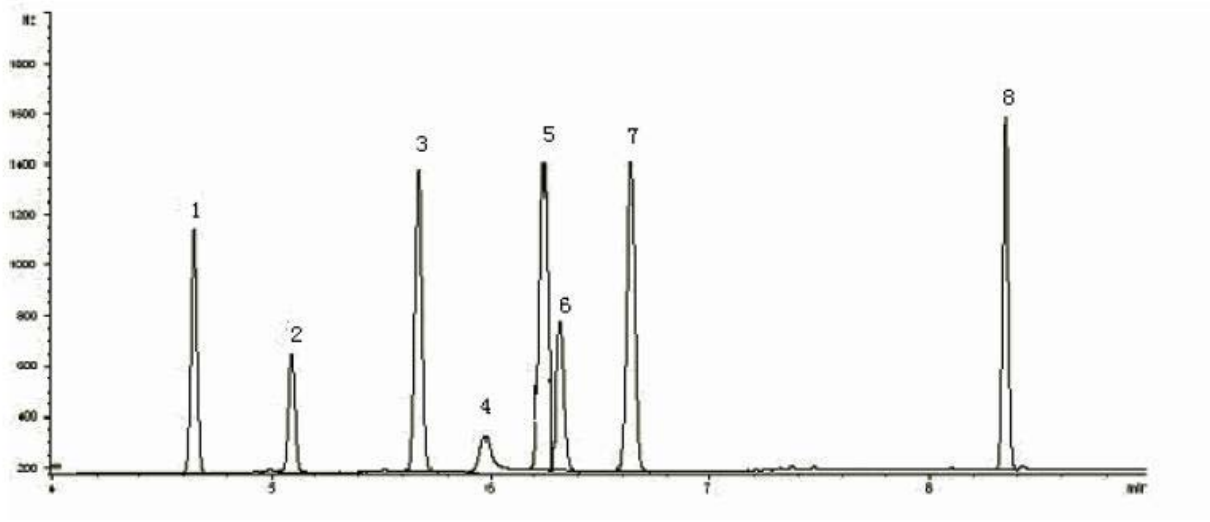

Figure 1 The peak sequences of test substances on HP-5 capillary column

Peak 1 – dichloromethane; Peak 2 – 1.1-dichloroethane;

Peak 3 – trichloromethane Peak 4 – bromopropane;

Peak 5 – 1.1-trichloroethane; Peak 6 – 1.2-dichloroethane;

Peak 7 – carbon tetrachloride; Peak 8 – 1.1.2-trichloroethane;

C.5.3 Test components in a qualitative sample:

Weigh out about 2g of the sample, after diluting with a suitable amount of dilution solvent (C.2.4). Conduct tests in accordance with the test conditions prescribed in C.5.1, and produce the determination of the test substances.

C.5.4 Determination of the relative correction factor of the test components

Weigh a certain amount (precise to 0.1mg) of the calibration compound as approved in C.5.3 for each test component and place into the sample preparation bottle (C.3.3). The weighed mass must be the same mass as the content of each substance in the test sample, and then weigh out the internal standard (C.2.5) which has a similar mass as the test compounds and put it into the same sample preparation bottle. Use the dilution solvent (C.2.4) to dilute the mixture (the diluted concentration must be within the linear range of the device detector. If the diluted concentration exceeds the stated range, then the diluting times must increase or use multiple dilution), seal the bottle and shake until the dilution is well mixed.

Under the same chromatographic conditions as the test sample, carry out parameter optimised treatment in accordance with C.5.1. Inject a suitable amount of the calibration compound into the gas chromatography and record the chromatogram.

The relative correction factor R_i of each test compound shall be determined by the formula (C.1) respectively:

$$R_i = \frac{m_{ci} \times A_{is}}{m_{is} \times A_{ci}} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (C.1)$$

Where:
R_i – the relative correction factor of the compound i;
m_{ci} – the mass of the compound i in the calibration mixture, g;
m_{is} – the mass of the internal standard in the calibration mixture, g;
A_{is} – the peak area of the internal standard;
A_{ci} – the peak area of the compound i.

Parallel test twice, take the mean value of the two test results as the R_i value. Its relative deviation must be less than 5%, retain three significant numbers.

C.5.5 Determination of the sample

C.5.5.1 Weigh out exactly 2 grams of the sample (precise to 0.1mg) and the internal standard which has the same mass as the test substances, put into the sample bottle (C.3.3). Use a suitable amount of dilution solvent (C.2.4) to dilute the sample, seal the bottle and shake the mixture well. After the device is steady, inject the 1.0μl sample and record the chromatogram. The content of each test substance in the sample is determined by the formula (C.2) respectively.

$$M_i = \frac{m_{is} \times A_i \times R_i}{m_s \times A_{is}} \times 100 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (C.2)$$

Where:
M_i – the mass fraction of the test component i in the sample, %;
R_i – the relative correction factor of the test component i;
m_{is} – the mass of the internal standard, unit of measurement is grams, g;
m_s – the mass of the sample, unit of measurement is grams, g;
A_{is} – the peak area of the internal standard;
A_i – the peak area of the test component i.

Parallel test twice, take the mean value of the two test results as the content of the test substance. Its relative deviation must be less than 5%.

C.5.5.2 The content of halohyrocarbon ($M_{halohyrocarbon}$) in the sample shall be determined by the formula (C.3):

$$M_{halohydrocarbon} = M_{dichloromethane} + M_{1,1dichloroethane} + M_{1,2\ dichloroethane} + M_{1,1,1\ trichloroethane} + M_{1,1,2\ trichloroethane} + M_{carbon\ tetrachloride} + M_{chloroform}$$

The test results must retain two significant digits.