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The methods of polybrominated biphenyls and polybrominated diphenyl ethers in automotive materials

汽车材料中多溴联苯（PBBs）和

多溴二苯酶（PBDEs）的检测方法

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"*Methyl Butenol Polyether*" and other 811 industrial standards are approved by the Ministry of Industry and Information Technology. In which - Chemical industry standard: 149 items; non-ferrous industry standard: 105 items; gold industry standard: 5 items; metallurgical industry standard: 15 items; building materials industry standard: 3 items; machinery industry standard: 39 items; aviation industry standard: 69 items; shipbuilding industry standard 53 items; automobile industry standard: 42 items; textile industry standard: 63 items; light industry standard: 59 items; petrochemical industry standard: 42 items; civil explosive industry standard: 1 item; electronics industry standard: 50 items; communications industry standard: 116 items.

Above chemical industry standards are published by Chemical Industry Press; textiles, non-ferrous and gold industry standards are published by China Standard Press; metallurgical industry standards are published by Metallurgical Industry Press; building materials industry standards are published by the Building Materials Industry Press; machinery industry standards are published by Machinery Industry Press; the aviation industry standards are published by China Aviation Integrated Technical Institute Organization; the shipbuilding industry standards are published by China Shipbuilding Technology and Economy Institute Organization; the automobile industry standards are published by the China Planning Press; light industry standards are published by China Light Industry Press; the petrochemical industry standard is published by the China Petrochemical Press; civil explosive industry standards are published by China Ordnance Industry Standard Institute Organization; electronic industry standards are published by the Ministry of Industry and Information Technology and electronics industry Standardization Institute organization; communication industry standards are published by the People's Posts and Telecom Press.

Annex: The Standard number, standard name and initial implementation date of 42 automobile industries.

Ministry of Industry and Information Technology of the People's Republic of China

October 17, 2013

Attachment:

Number, Name and Initial Implementation Date of the 42 Automobile Industry Standards

S/N	Standard No.	Standard Name	Replaced Standard No.	Implementation Date
355	QC/T 253-2013	Preparation Methods for Engine Model used in Motorcycles and Mopeds	QC/T 253-1998	2014-03-01
356	QC/T 682-2013	Seats Used in Motorcycles and Mopeds	QC/T 682-2002	2014-03-01
357	QC/T 229-2013	Technical Conditions for Rotor Pump of Motorcycles and Mopeds	QC/T 229-1997	2014-03-01
358	QC/T 952-2013	Disc Wheels for Passenger Car — Dimensional of Attachment on Hub		2014-03-01
359	QC/T 953-2013	Commercial Road Vehicles—Flat Attachment Wheel Fixing Nuts		2014-03-01
360	QC/T 954-2013	Commercial Vehicles—Flat Attachment Fixing Nuts—Test Methods		2014-03-01
361	QC/T 258-2013	Test Methods for the Intensity of Vehicle Wheels and Screw Base	QC/T 258-1998	2014-03-01
362	QC/T 199-2013	Vehicle Wheels - Balance Weight	QC/T 199-1995	2014-03-01
363	QC/T 326-2013	Numbering Rules for Automobile Standardized Parts	QC/T 326-1999	2014-03-01
364	QC/T 955-2013	Auto Leveling Device of Special Purpose Vehicle		2014-03-01
365	QC/T 956-2013	Transport Vehicle for Dry-mixed Mortar		2014-03-01
366	QC/T 957-2013	Cleaning Sweeper Truck		2014-03-01
367	QC/T 29104-2013	Method for Coding the Level of Contamination by Solid Particles of Special Purpose Vehicle Hydraulic System	QC/T 29104-1992	2014-03-01
368	QC/T 29105.3-2013	Sampling Methods of Testing Particulate Contamination of Hydraulic Oil of Special Purpose Vehicle Hydraulic System	QC/T 29105.3-1992	2014-03-01
369	QC/T 718-2013	Truck Mounted Concrete Pump	QC/T 718-2004	2014-03-01
370	QC/T 439-2013	Swept-body Dump Truck	QC/T 439-1999 QC/T 440-1999	2014-03-01
371	QC/T 935-2013	Kitchen Garbage Vehicle		2014-03-01
372	QC/T 939-2013	Technical Qualifications of Front Discharge Truck		2014-03-01
373	QC/T 457-2013	Ambulance	QC/T 457-2002	2014-03-01
374	QC/T 936-2013	Detachable Container Garbage Collector		2014-03-01
375	QC/T 937-2013	Guardrail Repair Car		2014-03-01
376	QC/T 940-2013	Exhibition Vehicle		2014-03-01
377	QC/T 958-2013	Performance Requirements and Bench Test Methods of Automobile Vacuum Pump		2014-03-01
378	QC/T 592-2013	Performance Requirements and Bench Test Methods for Hydraulic Brake Caliper Assembly	QC/T 592-1999	2014-03-01

379	QC/T 959-2013	Performance Requirements and Bench Test Methods for Mechanical Parking Brake Lever Assembly		2014-03-01
380	QC/T 960.1-2013	Road Vehicle- Hydraulic Braking Systems – Part 1: Double – Flare Pipes, Tapped Holes, Male Fittings and Tube Seats		2014-03-01
381	QC/T 961-2013	Performance Requirements and Bench Test Methods for Plastic Liquid Storage Tank of Hydraulic Braking Systems		2014-03-01
382	QC/T 949-2013	Specification for Audio Player on Board		2014-03-01
383	QC/T 951-2013	Circuits-breaker for Automobiles		2014-03-01
384	QC/T 490-2013	Drawings for Motor Vehicle Body	QC/T 490-2000	2014-03-01
385	QC/T 950-2013	Performance Requirement and Test of Heating Car Cushion		2014-03-01
386	QC/T 948-2013	Roof Load Carriers for Road Vehicles		2014-03-01
387	QC/T 946-2013	Strength Requirement and Test of Automobile Safe Belt Strap		2014-03-01
388	QC/T 945-2013	Passenger Vehicle Air-conditioning Unit		2014-03-01
389	QC/T 627-2013	Electronic Locks System for Motor Vehicles	QC/T 627-1999	2014-03-01
390	QC/T 662-2013	Vehicle Air Conditioner (HFC-134a) Receiver Dryer	QC/T 662-2000	2014-03-01
391	QC/T 947-2013	Technology Standards for Vehicle Auto-Dimming Rearview Mirror		2014-03-01
392	QC/T 941-2013	Test Methods of Mercury in Automobiles Materials		2014-03-01
393	QC/T 943-2013	Test Methods of Lead and Cadmium in Automotive Materials		2014-03-01
394	QC/T 942-2013	Test methods of Hexavalent Chromium in Automobiles Materials		2014-03-01
395	QC/T 944-2013	Determination of Polybrominated Biphenyls (PBBs) and Polybrominated Diphenyl Ethers (PBDEs) in Automobiles Material		2014-03-01
396	QC/T 938-2013	Test Specification of Protection for Pedestrians in the Event of a Collision		2014-03-01

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Foreword

This Standard was drafted in accordance with the rules given in GB/T 1.1-2009 *Directives for standardization - Part 1: Structure and drafting of standards*.

This Standard includes two analysis methods.

Method One “X-ray fluorescence spectrometry” was formulated on the basis of GB/Z 21277-2007 *Rapid screening of lead mercury chromium cadmium and bromine of regulated substances in electrical and electronic equipment-X-ray fluorescence spectrometry*.

Method Two “Gas chromatography-mass spectrometry (GC-MS)” was formulated on the basis of Annex A of IEC 62321:2008 Ed.1.0 *Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)* and GB/Z 21276-2007 *Determination of restricted substances - Polybrominated biphenyls and polybrominated diphenyl ethers in electrical and electronic equipment*.

Annex A and Annex B of this Standard are informative.

This Standard was proposed by and shall be under the jurisdiction of National Technical Committee on Automobile of Standardization Administration of China (SAC/TC 14).

Main drafting organizations of this Standard: China First Automobile Technology Co., Ltd., China Automotive Technology and Research Center, China Testing Technology Co., Ltd., SGS-CSTC Standards Technical Services Co., Ltd., Spectrum Test Technology Co., Ltd.

Main drafters of this Standard: Wang Huijuan, Liu Yanrong, Gao Junhua, Wang Jing, Hao Yanhong, Zhang Chunrong, Chen Liping, Guo Miao, Guo Yong, Li Weidong, Song Wei.

The methods of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in automotive materials

1 Scope

This Standard specifies the detection methods for PBBs and PBDEs in automotive materials.

"X-ray fluorescence spectrometry" is for X-ray fluorescence spectroscopy screening and rapid determination of bromine content in automotive materials.

The GC-MS method is applicable for the determination of PBBs and PBDEs in automotive materials by gas chromatography-mass spectrometry.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 8170, *Rules of rounding off for numerical values & expression and judgement of limiting values*

GB/T 30512-2014, *Requirements for Prohibited Substances on Automobiles*

GB/Z 21276-2007, *Determination of restricted substances - Polybrominated biphenyls and polybrominated diphenyl ethers in electrical and electronic equipment*

GB/Z 21277-2007, *Rapid screening of lead mercury chromium cadmium and bromine of regulated substances in electrical and electronic equipment-X-ray fluorescence spectrometry*

IEC62321:2008Ed.1.0, *Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers*

3 X-ray fluorescence spectrometry

3.1 Principle

Place the prepared sample in a sample chamber of an X-ray fluorescence spectrometer. Analyze the sample according to the selected test mode. Determine whether the content of bromine in the sample is qualified according to the screening limits of different samples, and whether it is necessary to carry out accurate determination.

3.2 Reagents and materials

3.2.1 Boric acid (HBO_3): analytical reagent, baking at 105°C for 1 h, storing in dryer

3.2.2 Standard substance containing bromine element

3.2.3 Liquid nitrogen: industrial grade

3.3 Apparatus and equipment

3.3.1 X-ray fluorescence spectrometer

3.3.2 Cutting machine

3.3.3 Grinder

3.3.4 Grinding machine: with tungsten carbide (WC) abrasives

3.3.5 Tableting machine: working pressure of not less than 20 MPa

3.3.6 Melting machine: working temperature of not less than 1150°C

3.4 Sample preparation

3.4.1 Sample preparation principle

3.4.1.1 The sample used for the test must cover the measurement window of the spectrometer.

3.4.1.2 The irradiated surface of the sample should be representative of the sample as a whole.

3.4.1.3 Pay attention to pollution prevention during sample preparation process.

3.4.2 Sample preparation method

4.3.5 Balance: a sense of 0.0001 g

4.3.6 Target quasi-screen (mesh diameter of 1 mm)

4.3.7 0.45 μm filter membrane

4.4 Sample preparation

The sample is made into small pieces of less than 10 mm x 10 mm x 10 mm by using scissors or a cutting machine (or other means). After the liquid chlorine is frozen, the sample shall be pulverized into particles having a particle size of less than 1.0 mm by a crusher (or by other equivalent grinding methods) (passing through a 18 # standard sieve). Mix it well.

4.5 Analysis steps

4.5.1 Soxhlet extraction

4.5.1.1 Add 70 mL of toluene (4.2.1) into the Soxhlet extractor. Extract 2h to clean the Soxhlet extractor, discard the extract.

4.5.1.2 Accurately weigh 0.1 g-0.2 g crushed sample, accurate to 0.0001 g. Put them into the fiber cable sleeve. After sealing with glass wool, place it in the Soxhlet extraction apparatus. Add 50 mL ~ 200 mL of toluene (4.2.1), internal standard solution (4.2.4), then 1 ~ 2 tablets of zeolite. Install the Soxhlet extraction device. Wrap it with aluminum foil to block light. Perform the heating extraction for more than 4h, at least 6 cycles per hour (if each cycle of sample requires about 2min ~ 3min, the heating extraction shall also need to extract for more than 2h). After the solution is cooled, use toluene (4.2.1) to set it to constant volume into a volumetric flask of appropriate volume. The solution passes through a 0.45 μm filter membrane and shall be used directly in the test step. If the concentration of the substance to be tested in the sample exceeds the range of the calibration curve, it shall appropriately dilute and then test. If the concentration of the substance to be tested in the sample is less than the range of the calibration curve, it shall use rotary evaporator or other means to concentrate the extract to appropriate volume before test.

NOTE If the solution is cloudy due to matrix, it can add 1 mL of methanol to improve. During the calculation, the difference in density between methanol and toluene (4.2.1) can be ignored.

4.5.2 Determination

4.5.2.1 Refer to gas chromatography - mass spectrometry conditions.

Gas chromatography-mass spectrometry parameters should be set to ensure that chromatographic determination of the measured components and other components can be effectively separated.

conditions specified in 4.5.2.1. Based on the ion peaks given in Tables A.1 and A.2, determine PBBs and PBDEs contained in the samples. Then according to peak area, calculate the contents of PBB and PBDEs from the calibration curve.

4.5.3 Blank test

Carry out the blank test with the sample.

4.6 Results calculation

Calculate the contents of PBB and PBDE in the samples according to formula (1):

$$X_i = \frac{(c_i - c_0) \times V_i \times d}{m_i} \quad \cdots\cdots (1)$$

where,

X_i - the content of polybrominated biphenyls and polybrominated diphenyl ethers in the samples, in mg/kg; value rounding in accordance with GB/T 8170;

c_i - contents of polybrominated biphenyls and polybrominated diphenyl ethers in sample extract, in mg/L;

c_0 - contents of polybrominated biphenyls and polybrominated diphenyl ethers in blank, in mg/L;

V_i - sample extract volume, in mL;

d - the dilution factor of the extract;

m_i - amount of sample, g.

4.7 Determination of low limit, recovery and precision

4.7.1 Determination of low limit

The minimum limits for the determination of PBB and PBDE in automotive materials of this method are given in Table A.1, Table A.2.

4.7.2 Recovery rate

The recovery rate of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in automotive materials is between 70% and 130%.

4.7.3 Precision

Under repeatability conditions, the absolute difference between the two independent test results obtained is not more than 20% of the arithmetic mean

Annex A

(Informative)

Molecular weight, quantitative and qualitative selection of ions and determination of low limit of polybrominated biphenyls and polybrominated diphenyl ethers

Table 1 Molecular weight, quantitative and qualitative selection of ions and determination of low limit of polybrominated biphenyls

No.	Compound name	Formula	Molecular weight	Characteristic ions amu				Determination of low limit mg/kg
				Quantitative	Qualitative			
1	Brominated biphenyls	$C_{12}H_9Br$	233.1	231.9	152.2	232.0	233.9	5
2	Dibromobiphenyl	$C_{12}H_8Br_2$	312.0	311.8	152.2	309.8	313.8	5
3	Tribromobiphenyl	$C_{12}H_7Br_3$	390.9	389.8	230.0	387.8	391.8	5
4	Tetrabromobiphenyl	$C_{12}H_6Br_4$	469.8	309.8	307.8	309.8	467.7	5
5	Pentabromobiphenyl	$C_{12}H_5Br_5$	548.7	387.7	385.7	545.6	549.6	5
6	Hexabromobiphenyl	$C_{12}H_4Br_6$	627.6	467.6	465.6	625.5	627.5	5
7	Heptabromobiphenyl	$C_{12}H_3Br_7$	706.5	545.6	543.6	703.4	705.4	5
8	Octabromobiphenyl	$C_{12}H_2Br_8$	785.4	625.5	623.5	627.5	783.4	5
9	Nonyl bromide	$C_{12}HBr_9$	864.3	703.4	701.4	705.4	863.4	5
10	Decabromodiphenyl	$C_{12}Br_{10}$	943.2	783.3	382.6	785.3	943.1	5

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