

Analytical Method for Restricted Substances in Industrial Products Regulated by EU

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In recent years, advanced regulations concerning restrictions on the use of hazardous substances have been enforced in the European Union (EU) as environmental pollution control acts. Subsequent to the RoHS (Restriction of the use of certain Hazardous Substances in electrical and electronic equipment) directive for electric and electronic equipment, restrictions on the use of hazardous substances are being examined in the field of all industrial products, where REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) regulations have been enforced. The use of fifteen substances of very high concern has been restricted by the REACH regulations.

The European Commission (EC) has submitted proposals to amend the RoHS directive and one proposal is to consider adding four substances to the list of restricted substances. The importance of hazardous substances management in industrial products is increasing more and more from such a background.

This paper describes testing methods for restricted substances in industrial products regulated by the EU.

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Introduction

The World Summit on Sustainable Development was held in Johannesburg in 2002, taking advantage of the opportunity of the adoption of "Agenda 21," the action plan required for implementing sustainable development in the 21st Century from the United Nations Conference on the Environment (Earth Summit) held in Rio de Janeiro in 1992. In addition, the "Strategic Approach to International Chemical Management" was adopted in Dubai in 2006, and it became apparent that we would move toward managing chemical substances under the keywords of "preventative approach" based on "risk assessments" by "2020." The Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) put in force by the European Union (EU) in July 2006 began with this background, and management of chemical substances in manufactured products expanded globally. The trend is for an increase in the number of targeted substances. Following RoHS, the Stockholm Convention on Persistent Organic Pollutants, Registration,

Evaluation, Authorization and Restriction of Chemicals (REACH) and other regulations managing chemical substances were put into effect.

1. Rotterdam Convention

The Rotterdam Convention on The Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (often referred to as the 'Rotterdam Convention') was adopted in September 1998. The purpose of the Rotterdam Convention is to promote the exchange of information about the properties of certain hazardous chemical substances, to provide procedures for informed consent by various countries regarding the export and import of these chemical substances, as well as to notify the signatory nations of that consent in order to protect the health of human beings and the environment from potential harm. In the Rotterdam Convention, the signatory nations decided to make mandatory the registration of their intentions to import 40 chemical substances delineated in Appendix III of the Convention and also the assurance of the signato-

ry exporting nations to adhere to the import intentions of the importing signatory nations. In February 2009 tributyltin compounds were a new addition to the Appendix.

2. RoHS¹⁾

RoHS is an abbreviation for “Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment,” and it was put into force on July 1, 2006. This is a regulation to restrict the use of certain hazardous substances to reduce the environmental impact from electric and electronic equipment waste. The substances targeted by the regulation are lead, mercury, cadmium, hexavalent chromium and two specific brominated flame retardants (polybrominated biphenyls and polybrominated diphenyl ethers). The maximum allowable concentration for lead, mercury, hexavalent chromium and the two types of brominated flame retardant is 0.1% by weight and for cadmium it is 0.01% by weight. The salient feature of RoHS is shifting the management of chemical substances from the environment to manufactured products. RoHS, which started with the EU, has spread throughout the world with a Chinese version, a Korean version, a Turkish version and other similar regulations. The outlook is for promulgation of the US version of RoHS in July 2010.

In addition, the European Commission proposed a revised version of RoHS in December 2008. New priority evaluations have been proposed for four substances: hexabromocyclododecane, 2-ethylhexyl phthalate and benzyl butyl phthalate and dibutyl phthalate in the proposed revised version of RoHS including six existing substances. Therefore, these four substances will probably be designated as prohibited substances under RoHS.

3. REACH Regulations^{1), 2)}

REACH is an acronym for “Registration, Evaluation, Authorization and Restriction of Chemicals”, and it is a comprehensive EU regulation for the registration, evaluation, authorization and restriction of chemical substances. Unlike RoHS, which targets only certain chemical substances in electrical and electronic equipment, REACH targets all new and existing chemical substances other than pharmaceutical agents, agricultural chemicals and food additives. The purposes are to “maintain a high level of human health and the environment,” to “promote alternative methods for

evaluating the harmfulness of substances (meaning alternatives to animal tests),” to “strengthen the competitiveness of EU enterprises” and to “promote the free movement of substances in the EU market.” REACH comprehensively manages chemical substances, and the following salient features can be cited.

- Management of existing chemical substances and new chemical substances by the same system;
- Sharing and cooperative submission of registration information;
- Shift of responsibility for risk evaluation to the industry side;
- Safety management through the supply chain.

Furthermore, REACH targets the regulation of substances of very high concern in products. Substances of very high concern are selected from substances that fall under the standards for carcinogenic, mutagenic and reprotoxic substances (CMR), persistent, bioaccumulative and toxic substances (PBT), very persistent and very bioaccumulative substances (vPvB), endocrine disrupting chemicals, etc. In October 2008, the European Chemicals Agency announced the 15 substances given in **Table 1** as substances of high concern.

Table 1 Substances of very high concern in REACH regulation

	Substances name	Reason for proposing
1	Anthracene	PBT*
2	4,4'-Diaminodiphenylmethane	CMR**
3	Dibutyl phthalate	CMR**
4	Cobalt dichloride	CMR**
5	Diarsenic pentaoxide	CMR**
6	Diarsenic trioxide	CMR**
7	Sodium dichromate dihydrate	CMR**
8	Musk xylene	vPvB***
9	Bis(2-ethyl(hexyl)phthalate	CMR**
10	Hexabromocyclododecane	PBT*
11	Alkanes, C10 ~ 13, Chloro (Short Chain Chlorinated Paraffines)	CMR**
12	Bis(tributyltin)oxide	PBT*
13	Lead hydrogen arsenate	CMR**
14	Triethyl arsenate	CMR**
15	Benzyl butyl phthalate	CMR**

* : Persistent, Bioaccumulative, Toxic

** : Carcinogens, Mutagens, toxic to Reproduction

*** : very Persistent, very Bioaccumulative

Furthermore, the European Chemicals Agency cited the 15 substances in **Table 2** as early candidates for the next set of substances of very high concern (as of October 2009), and the outlook is for gradual addition of substances of very high concern in the future.

Table 2 Potential substances of very high concern in REACH regulation

	Substances name	Reason for proposing
1	Anthracene oil	PBT
2	Anthracene oil, anthracene, paste, distin. lights	PBT
3	Antracene oil, anthracene, paste, antracene fraction	PBT
4	Anthracene oil, antracene-low	PBT
5	Anthracene oil, anthracene paste	PBT
6	Coal tar pitch, high temperature	PBT and CMR
7	Acrylamide	CMR
8	Aluminosilicate, refractory ceramic fibres	CMR
9	Zirconia aluminosilicate, refractory ceramic fibres	CMR
10	2,4-Dinitrotoluene	CMR
11	Diisobutyl phthalate	CMR
12	Lead chromate	CMR
13	Lead chromate molybdate sulphate red (C.I. Pigment Red104)	CMR
14	Lead chromate yellow(C.I. Pigment Yellow34)	CMR
15	Tris(2-chloroethyl)phosphate	CMR

PBT and CMR are same meaning as Table 1

According to Article 33 of the REACH regulations, information must be transmitted to users or a response must be given on content information within 45 days when the content of a substance of very high concern exceeds 0.1% by weight in a product. Therefore, we must get a grasp on the information about the substances of very high concern in products subject to REACH. Analysis plays an important role as a means for doing this.

In this paper, we will introduce an analytical method for seven of the 15 substances currently stipulated as REACH substances of very high concern that are

organic components and three of the 15 candidates for substances of very high concern that are organic components. We will also introduce a simultaneous analytical method for hexabromocyclododecane, which has been proposed for priority evaluation in the revised RoHS directive proposal, and tetrabromobisphenol A, the harmful nature of which causes concern even though it is not targeted by RoHS. We will also introduce a precision analytical method for tributyltin compounds, which were added to the Rotterdam Convention in February 2009.

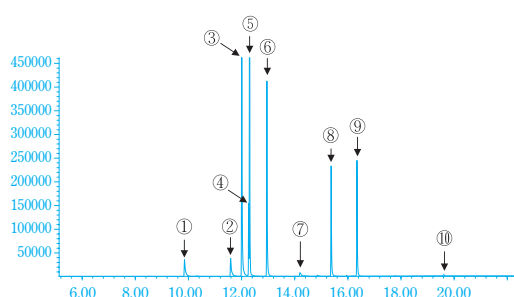
Test Methods for the Targets of the Various Regulations

1. Test methods for REACH substances of very high concern

REACH substances of very high concern can be measured using a gas chromatograph-mass spectrometer (GC-MS). The targets for measurement by this method are a total of 10 substances, including three substances cited as candidates for addition to the substances of very high concern (diisobutyl phthalate, tris (2-chloroethyl) phosphate and 2,4-dinitrotoluene) in addition to substances of very high concern (anthracene, musk xylene, dibutyl phthalate, 2-ethylhexyl phthalate, benzyl butyl phthalate, 4,4'-diaminodiphenylmethane and hexabromocyclododecane).

(1) Measurement methods

The first step toward measurements is extracting the target components from the industrial product. Here, we used ultrasonic extraction using an organic solvent. At this time, it was necessary to increase the surface area of the samples by freeze-crushing and forming a fine powder to increase the extraction efficiency. The extracted liquid was measured in a GC-MS. **Fig. 1**



- ① 2,4-Dinitrotoluene
- ② Tris(2-chloroethyl)phosphate
- ③ Anthracene
- ④ Musk xylene
- ⑤ Diisobutyl phthalate
- ⑥ Dibutyl phthalate
- ⑦ 4,4-Diaminodiphenylmethane
- ⑧ Benzyl butyl phthalate
- ⑨ Bis(2-ethylhexyl)phthalate
- ⑩ Hexabromocyclododecane

Fig. 1 Typical TIC chromatogram of substances of very high concern by GC-MS

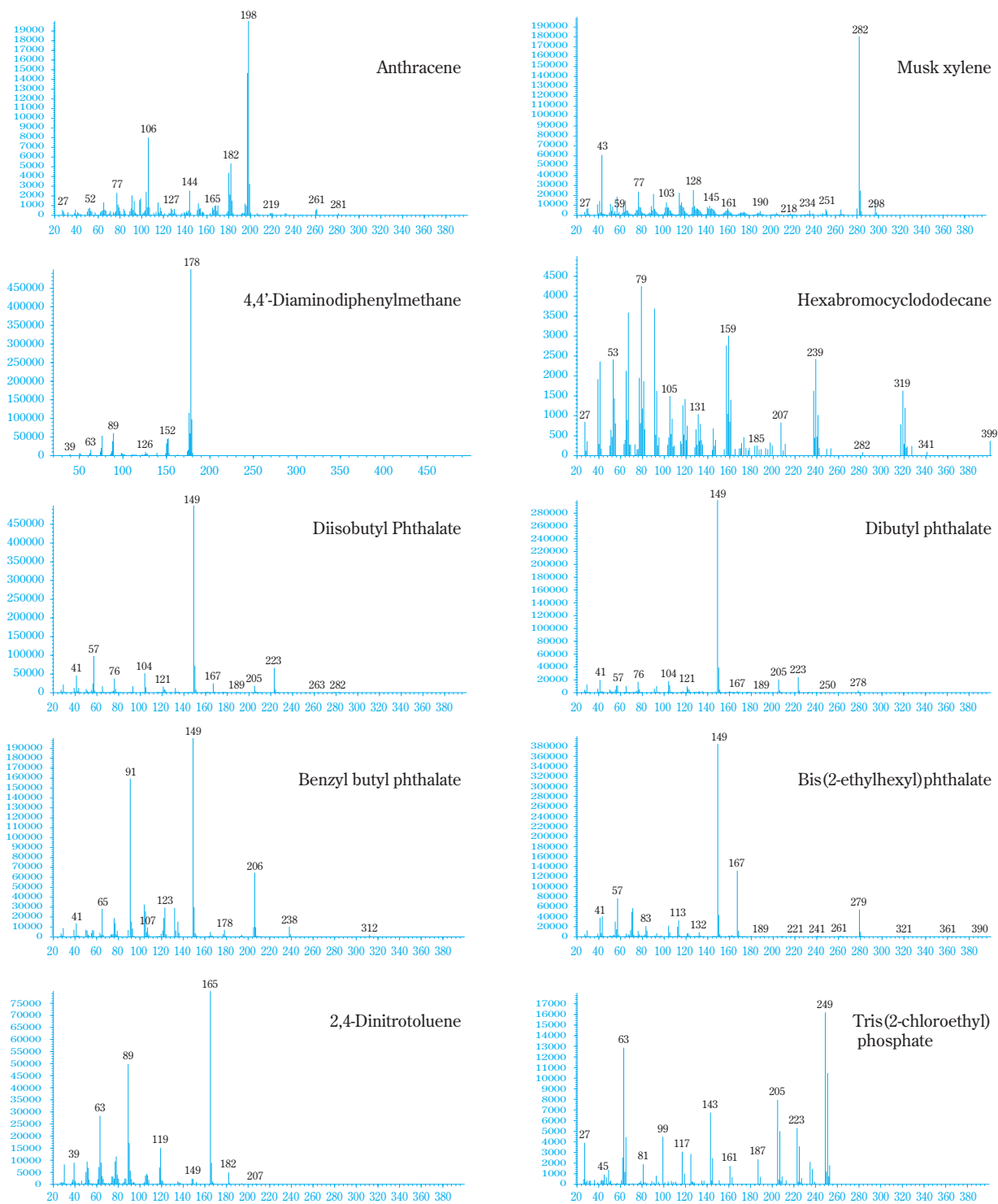


Fig. 2 Mass spectra of substances of very high concern

shows the GC-MS chromatogram and **Fig. 2** the mass spectrum for each substance.

Quantitative determination was carried out by a comparison with the peak surface area values for a standard substance (equivalent to a concentration of 0.01% by weight in the sample). As a result of the quantitative determination, peak identification was carried out when detection exceeded a lower limit of quantitation.

The identification was carried out from a comparison of retention time in the chromatogram and the monitor ion intensity. Furthermore, measurements were also made in SCAN mode, and it is possible to identify the REACH substances comparing spectral patterns from these with the spectral patterns for the standard substance shown in **Fig. 2**.

Table 3 Result of determination of substances of very high concern in industrial product (wt. %)

Product No.	material	Anthracene	Musk xylene	4,4'-Diaminodiphenylmethane	Hexabromo cyclododecane	Dibutyl phthalate	Benzyl butyl phthalate	Bis (2-ethylhexyl) phthalate	Diisobutyl Phthalate	2,4-Dinitrotoluene	Tris (2-chloroethyl) phosphate
1	Polystyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
2	Polystyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
3	PET	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
4	PET	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.0	< 0.01	< 0.01	< 0.01
5	Polypropylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
6	Polypropylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
7	Polypropylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
8	Polypropylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
9	Polypropylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
10	Polypropylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
11	Polypropylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
12	ABS	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
13	ABS	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
14	ABS	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
15	PVC	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	14	2.1	0.024	< 0.01	< 0.01
16	PVC	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	5.0	< 0.01	< 0.01
17	Polyester and Polyethylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.020	< 0.01	< 0.01
18	Styrene acrylonitrile	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
19	-	< 0.01	0.030	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

(2) Results of monitoring surveys

We determined the quantities of the organic components in industrial products currently on the market. In this survey, measurements targeted a total of 19 materials such as polystyrene and acrylonitrile butadiene styrene (ABS resin). The results are given in **Table 3**. According to this, amounts of substances of very high concern of 0.1 % by weight or greater were detected in some materials.

2. Test methods for brominated flame retardants

Materials and components that contain organic polymer materials like plastics and rubber are used in many consumer electronic products, automobiles, automated office equipment, etc., which are indispensable to our comfort in life. In addition to these organic polymer materials having superior workability and insulating properties, they contribute to weight reduction in materials and reductions in prices. In addition to these basic properties, the amounts that are used are increasing because of improvements in heat resistance and flame retardant properties.

Inorganic, bromine, chlorine and phosphorous based flame retardants that give organic polymer materials flame resisting properties are used. Of these the ones most commonly used in Japan are inorganic

based, followed by bromine and phosphorous based.³⁾ In addition to the fact that there is a fear of harmful effects on living organisms with most of the chlorine and bromine based flame retardants, they are dispersed on a global scale because they are used in various materials, and they have attracted attention as substances which are feared to be causing serious environmental pollution. In addition, since there is a possibility that these flame retardants generate dioxins when they are burned, there is an intensifying of trends to regulate their use internationally. RoHS specifies polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) as specific brominated flame retardants, and demands that they be of the regulation value or lower.

Hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA) have attracted attention as compounds that are alternatives for PBB and PBDE because of this situation. However, there has been an intensifying of trends to regulate these two substances in recent years, and as was discussed at the beginning of this paper, HBCDD is one of the REACH substances of very high concern and it is a substance proposed for priority evaluation in the revised RoHS directive proposal. In addition, TBBPA has been cited as a substance targeted for regulation in the Norwegian RoHS

proposal, and it is a substance that is attracting attention in the trends toward regulation.

The samples targeted in these tests are diverse, from products formed from raw materials to composite materials, and since the properties and conditions as well as the inhibiting components measured differ according to the sample, the same preparation methods cannot always be applied. Here we will introduce a preparation method for HBCDD and TBBPA in manufactured products.

(1) Preparation method

When measurements are made, the target component in the product must be extracted from the product. Manabe et al.^{4), 5)} use reprecipitation methods, ultrasonic extraction methods, Soxhlet extraction, etc. to extract certain brominated compounds (PBB and PBDE) from resins. We confirmed that ultrasonic extraction can sufficiently extract the target components as a preparation method for HBCDD and TBBPA, and we used this.

Next, contaminants originating in the samples that coexist with the target component in the extracted solution must be eliminated and it must be purified to a solution with just the target substance. Sulfuric acid treatment is often used for this purification method. This method decomposes the polymers and other contaminants that are included in the sample using sulfuric acid, reduces the size of the molecules, increases polarity, moves the contaminants to the sulfuric acid layer and eliminates them. However, complete elimination is impossible when the contaminants exhibit the same behavior as the target component. In such cases, column chromatography that carries out adsorptive separation of the contaminants using activated silica gel, etc., is effective.⁶⁾ In these measurements, we obtained a high level purification effect with sulfuric acid treatments, and in addition, the target components did not break down because of the sulfuric acid, so we selected the sulfuric acid treatment.

(2) Measurements and quantitative determination

When organic components are measured, a GC-MS is generally used. However, the following problems have been pointed out in measurements of HBCDD and TBBPA using GC-MS.

– There is no separate quantitative determination for isomers of HBCDD;

– Conversion to a derivative using a trimethylsilyl (TMS) reagent is required for TBBPA measurements, and that operation is complicated;

– If the TMS reagent for forming the TBBPA derivative is present in the measurement solution, there is a reduction in the HBCDD recovery rate, and it is difficult to make simultaneous quantitative determinations for TBBPA and HBCDD (Fig. 3).

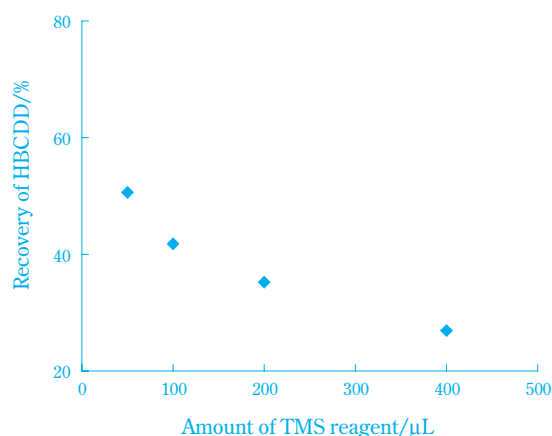


Fig. 3 Recovery of HBCDD with TMS reagent

Liquid chromatography/tandem mass spectrometry (LC-MS/MS) has attracted attention as an alternative to GC-MS.^{6), 7)} With the dissemination and developments in LC-MS/MS in recent years, there have been many announcements of measurement examples using LC-MS/MS. We made measurements using LC-

Table 4 Analytical condition for determination of HBCDD and TBBPA

LC system	ACQUITY UPLC system (Waters)			
MS/MS system	Qtrap3200 (Applied Biosystems)			
Column	SUMIPAX ODS D-210MS 5μm (2mm I.D. × 5cm)			
Mobile phase				
A	Acetonitrile			
B	water			
Gradient				
Time/min	0	20	30	40
A conc./%	5	5	100	100
B conc./%	95	95	0	0
Flow rate	0.2mL/min			
Column temp.	40°C			
Injection volume	5μL			
Ionization method	ESI			
Mode	MRM (Multiple Reaction Monitoring)			
Polarity	Negative			
Monitoring time	40min			

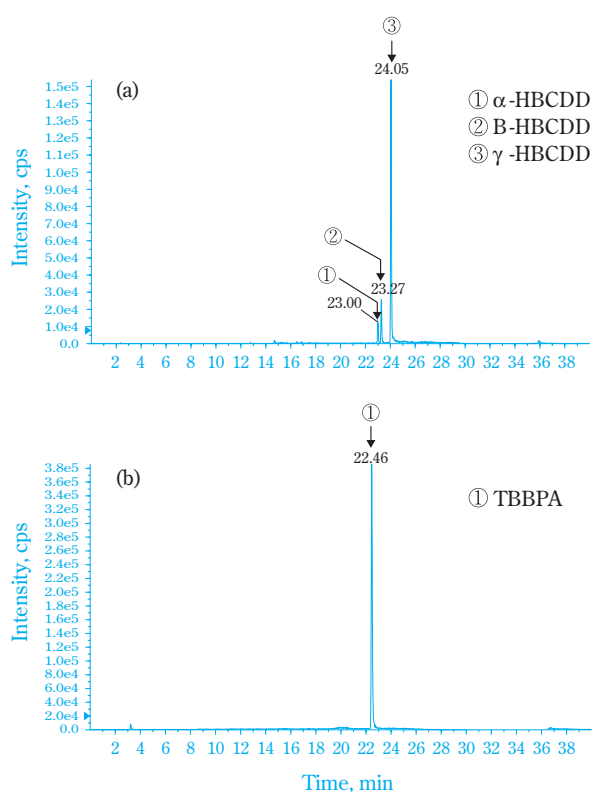


Fig. 4 Typical MRM chromatograms of HBCDD and TBBPA by LC-MS/MS
(a) HBCDD, (b) TBBPA

MS/MS here. The measurement conditions are shown in Table 4, and LC-MS/MS chromatograms are shown Fig. 4. From these results, it was possible to separate the alpha, beta and gamma isomers of HBCDD. The calibration curve exhibited good linearity in a concentration range of 5 ng/mL to 1000 ng/mL.

(3) Recovery tests

The standard substances for HBCDD and TBBPA were added to commercial polystyrene, and recovery tests were carried out. As a result, we obtained good results with the recovery rate for both HBCDD and TBBPA being 90% or more and were able to confirm the validity of this analytical method.

3. Test method for organotin compounds

Organotin is the name for compounds where one to four alkyl groups are bonded to tin, and they are widely used as stabilizers and catalysts for polyvinyl chloride, glass coating agents, etc. Approximately 1 to 1.5% of dibutyltin and dioctyltin compounds and recently dimethyltin compounds are added to polyvinyl chloride products in particular to prevent decomposition due to heat and light.

Among these organotin compounds, tributyltin compounds are very toxic, and in particular, tributyltin oxide is specified as a REACH substance of very high concern. As was previously mentioned, tributyltin compounds were added to the PIC list for the Rotterdam Convention on the prior informed consent procedure for importing and exporting hazardous chemicals on February 1, 2009. Therefore, we must get a grasp on the content information for tributyltin compounds in manufactured products.

The samples that are targets of measurement for tributyltin compounds are also diverse, ranging from products formed from raw materials to composite materials. In addition, Kawamura⁸⁾ and Ohno⁹⁾ have presented examples of measurements of tributyltin compounds for manufactured products. We will show a measurement method targeting manufactured products here.

(1) Preparation method

Ohno⁹⁾ has reported on a method for extracting the target component from industrial products where one to two drops of hydrochloric acid are added to an acetone/hexane (3:7) solution, the product left at rest overnight in this at 37°C and the target component eluted.

In addition, there is also a method where, after the polymer components are precipitated and eliminated by polymer reprecipitation, an aqueous solution of hydrochloric acid is added, and the organotin components are extracted using liquid-liquid extraction. Recently, there has been an announcement of a method of extraction using microwaves.¹⁰⁾ Various methods have been proposed in this manner, but here we selected the reprecipitation method where the industrial product is first completely dissolved.

Next, as with the brominated compounds, a similar purification of the extracted solution is required for measurements of organotin. However, unlike the brominated compounds, organotin compounds decompose when they come into contact with sulfuric acid, so sulfuric acid treatment cannot be used. Mizuishi et al.¹¹⁾ have carried out purification using a column chromatography treatment that makes use of activated florisil when measuring tributyltin compounds in environmental samples. Therefore, we also carried out purification with a column chromatography using florisil in this method. A chromatography tube was packed with florisil, and conditioning was carried out

using a diethyl ether/hexane solvent. After loading the sample, the tributyltin compounds were eluted with the diethyl ether/hexane solvent. Fig. 5 shows the results of column chromatography elution. Since the tributyltin compounds can be eluted in this manner with 30 mL, the amount of solvent when eluting them was set at 30 mL.

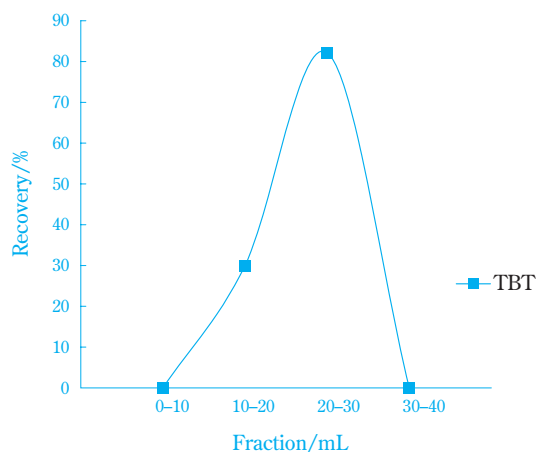


Fig. 5 Elution pattern of TBT from column chromatography

(2) Measurements and quantitative determination

Measurements of tributyltin compounds are often made by carrying out ethylation or propylation and measuring them using GC-MS. However, if contaminants that could not be eliminated in preparation remain, the reaction is insufficient for derivatization. In addition, when organotin compounds other than tributyltin compounds are also present, there are problems such as insufficient derivatization. Therefore, we investigated a method using LC-MS/MS without carrying out derivatization here. Chromatograms from measurements using LC-MS/MS are shown in Fig. 6. Therefore we found that it was possible to measure tributyltin compounds with direct LC-MS/MS measurements without derivatization. For quantitative determination, a standard substance with a stable isotope of tributyltin (surrogate substance) was used as the internal substance. The calibration curve for the derivative exhibited good linearity in a concentration range of 5 ng/mL to 1000 ng/mL.

(3) Recovery tests

The standard substance was added to a commercial polystyrene resin and the preparation method was carried out. As a result, we obtained good results with a

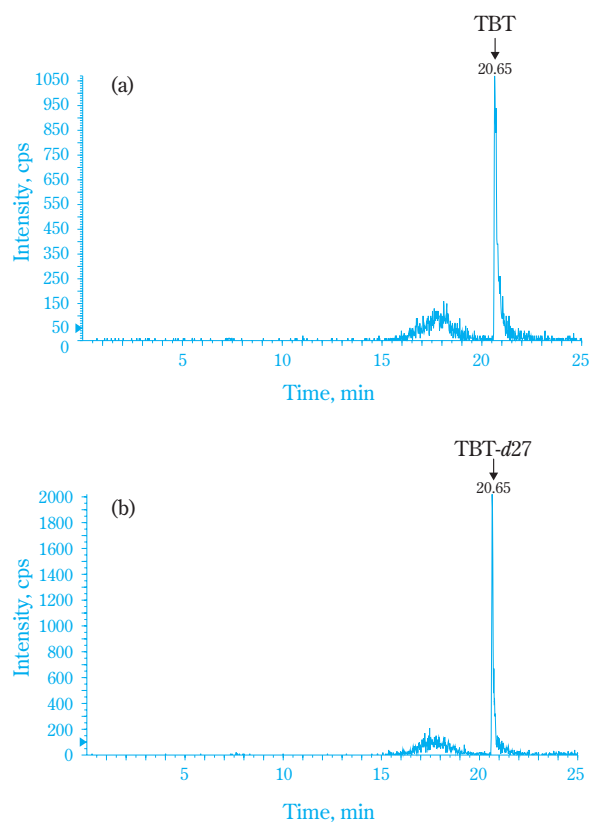


Fig. 6 Typical MRM chromatograms of TBT compound by LC-MS/MS (a)TBT, (b)TBT-*d*27

recovery rate of 90% and confirmed the validity of this test method.

4. Test method for specific aromatic amines produced from azo dyes and pigments

Azo dyes and pigments, which are widely used as colorants for various products, are known to bring about cleavage reactions of the azo groups ($-N=N-$) in the structure and produce carcinogenic aromatic amines. EN14362, which is a European standard, targets for regulation the 22 aromatic amines designated as harmful out of the amines that are produced (Table 5). In Germany, it has been decided that “the manufacture, import and sale of articles for everyday use that include azo dyes and pigments that produce specific aromatic amines by cleavage of one or more azo groups are prohibited” in the German regulations for articles for everyday use. In addition, the specific amines that are produced by azo dyes and pigments are also specified as a target (2-A: Targets of Evaluation) in the Joint Industry Guide (JIG) drafted by electric and electronics groups in Japan, the United States and Europe. They have also been cited as sub-

Table 5 Specific aromatic amines in EN14362

Specific aromatic amines	
1	4-Aminodiphenyl
2	Benzidine
3	4-Chloro-o-toluidine
4	2-Naphthylamine
5	o-Aminoazotoluene
6	2-Amino-4-nitrotoluene
7	p-Chloroaniline
8	2,4-Diaminoanisole
9	4,4'-Methylenedianiline
10	3,3'-Dichlorobenzidine
11	3,3'-Dimethoxybenzidine
12	3,3'-Dimethylbenzidine
13	4,4'-Methylenedi-o-toluidine
14	p-Cresidine
15	4,4'-Methylenebis(2-chloroaniline)
16	4,4'-Oxydianiline
17	4,4'-Thiodianiline
18	o-Toluidine
19	4-Methyl-m-phenylenediamine
20	2,4,5-Trimethylaniline
21	o-Anisidine
22	4-Amino azo benzene

stances for which use is prohibited in the green procurement standards for various companies.

Because of this, it is important to accurately quantify the specific aromatic amines from industrial products using azo dyes and pigments. Here, we will introduce a method for measuring the specific aromatic amines from industrial products.

(1) Preparation method

There are no reports of methods for measuring azo dyes and pigments from industrial products. Therefore, we referred to the method in EN14362-1 which describes a method for extraction from cloth and other fibers.¹²⁾ This method does the extraction with water, carries out the cleavage reaction with sodium dithionite and carries out the purification with a diatomaceous earth column. When we carried out this preparation method using the standard substance for the specific aromatic amines, we had a low recovery rate for almost all of the specific aromatic amines with the EN14362-1 method. The following two points can be cited as causes of this.

– Since extremely low values were shown for diamines with low molecular weights, such as 2,4-diaminoanisole and 4-methyl-m-phenylenediamine,

the amines were oxidized during the measurement operation.

– 4-aminoazobenzene was decomposed into aniline and 1,4-phenylenediamine, but neither of these compounds can be measured by this method.

Furthermore, in addition to the problems described above, the method in EN14362-1 carries out the extraction in an aqueous solution, so industrial products do not precipitate, and extraction using ultrasonic extraction methods is not desirable. Furthermore, there are problems such as presuming that azo group cleavage reactions will not progress in pigment components that are insoluble in water.

Therefore, we carried out investigations into a new measurement method that would solve these problems. First of all, we investigated solutions for the two problems described above. We examined protection of the amino groups for the oxidation of the specific aromatic amines. There are the methods of acylation, benzoylation, silylation and forming a Schiff's base for the method for protecting the amino groups. We chose

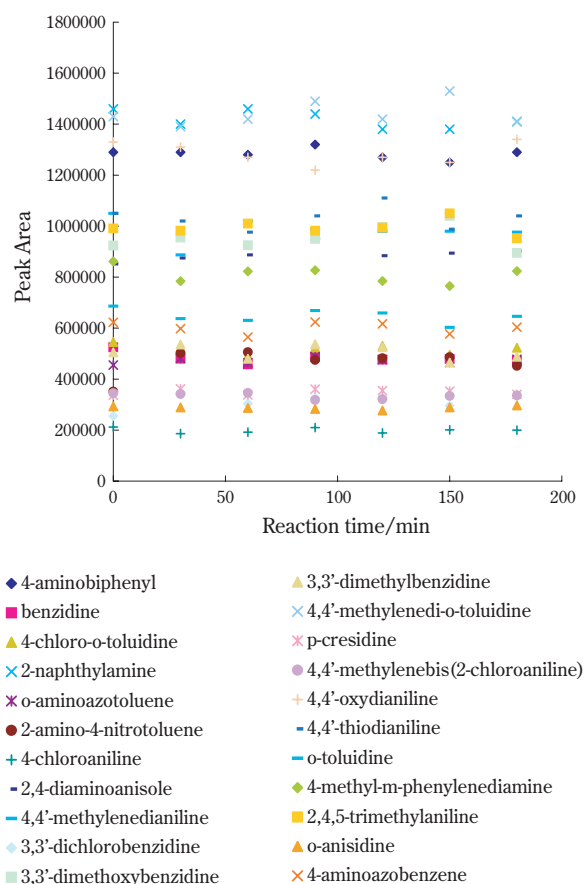


Fig. 7 Effect of reaction time in derivatized reaction of specific aromatic amines

acylation. The acylation reaction is carried out by adding an organic acid and anhydrous organic acid to the sample solvent. The results of investigations into the reaction time for the acylation reaction of the specific aromatic amines are shown in Fig. 7. The acylation reaction was completed within 30 minutes following the addition of the standard substance. In addition, it was also possible to measure aniline and 1,4-phenylenediamine using this method.

Next, since recovery from industrial products is not possible with water extraction, we investigated whether it would be possible to change to organic solvent extraction. When carrying out extraction with an organic solvent, the cleavage method is a problem.

The reaction for the sodium dithionite used in the EN14362-1 method does not progress easily in an organic solvent. Since Gowda¹³⁾ uses zinc powder and an organic acid in azo group cleavage reactions, we investigated whether this method could be applied. When zinc powder and an organic acid were added to the organic solution, dyes added and the cleavage reaction investigated, the cleavage reaction was possible in the organic solvent.

Furthermore, since we used zinc powder and an organic acid for the cleavage reaction in the two methods described above and used an organic acid and anhydrous organic acid for the acylation reaction, we thought it might be possible to carry out these reactions at the same time. The standard substance for the specific aromatic amines was added to the organic solvent, an organic acid, anhydrous organic acid and zinc

powder added and ultrasonic extraction carried out. The results are shown in Fig. 8. A recovery rate higher than that for the EN14362-1 method was obtained with this newly proposed method.

In addition, the results of carrying out the same operation with dyes added are shown in Table 6. In these results, a recovery rate higher than that with the EN14362-1 method was obtained when the standard substance was used.

Table 6 Recovery of specific aromatic amines from azo dyes

Azo dye	Specific aromatic amine derived from azo dye	Recovery/%	
		Inhouse	EN14362
Direct Red 28 (Congo Red)	Benzidine	106	26
Direct Blue1	3,3'-Dimethoxybenzidine	58	33
Direct Blue2	3,3'-Dimethylbenzidine	50	19
Bismarck Brown R	4-Methyl-m-phenylenediamine	42	3.1
Ponceau 3R	2,4,5-Trimethylaniline	116	32
Sudan R	o-Anisidine	112	13
Sudan III	Aniline	116	10
	1,4-Phenylenediamine	118	0.2

(2) Measurements and quantitative determination

In the conventional EN14362-1 method, quantitative determination was carried out by GC-MS, but here, we used LCMS/MS which is capable of analysis with high sensitivity in a short time. The calibration curve exhibited good linearity in a range of 5 ng/mL to 1000 ng/mL.

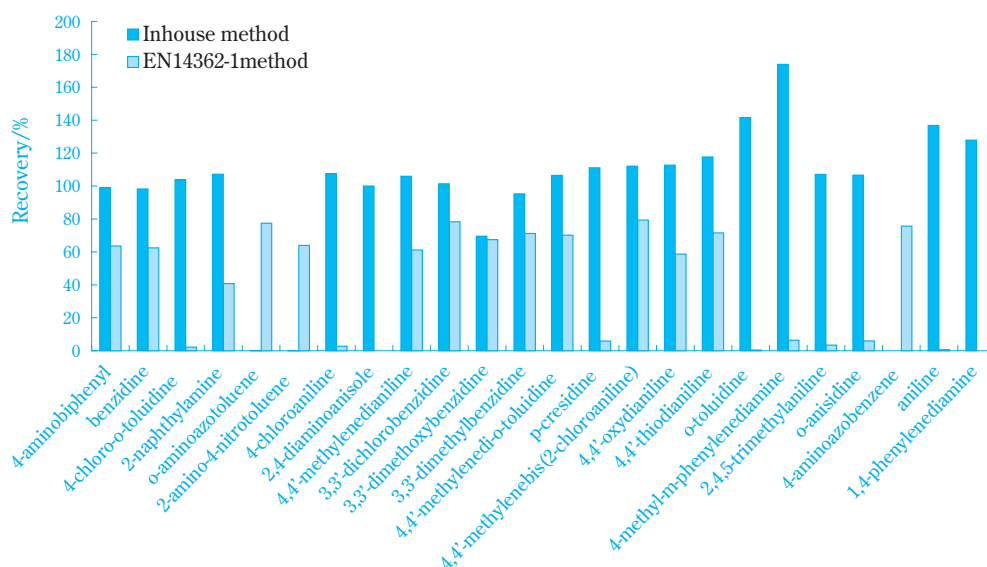


Fig. 8 Comparison of recovery of between Inhouse and EN14362-1 method

(3) Recovery tests

Dyes and pigments were added to a commercial polystyrene resin and the preparation method was carried out. The results of the recovery tests for the dyes are shown in **Table 7**, and the results of the recovery tests for the pigments are shown in **Table 8**.

Table 7 Recovery of specific aromatic amines from azo dyes in polystyrene

Azo dye	Specific aromatic amine derived from azo dye	Recovery/%	
		Inhouse	EN14362
Direct Red 28 (Congo Red)	Benzidine	61	–
Direct Blue1	3,3'-Dimethoxybenzidine	27	–
Direct Blue2	3,3'-Diethylbenzidine	31	–
Sudan IV	o-Toluidine	102	0
Bismarck Brown R	4-Methyl-m-phenylenediamine	14	–
Ponceau 3R	2,4,5-Trimethylamine	79	–
Sudan R	o-Anisidine	108	–
Sudan III	Aniline	119	0
	1,4-Phenylenediamine	108	0

Table 8 Recovery of specific aromatic amines from azo pigments in polystyrene

Azo pigment	Specific aromatic amine derived from azo pigments	Recovery/%	
		Inhouse	EN14362
Benzidine Yellow (Pigment Yellow14)	3,3'-Dichlorobenzidine	40	0
Pigment Red (Pigment Red1)	1,4-Phenylenediamine	77	–
Pigment Red4	2-Chloro-1,4-phenylenediamine	89	0
Pigment Yellow 1	4-Methyl-o-phenylenediamine	67	0

A recovery rate higher than that for the EN1436-1 method was obtained for both, and we were able to confirm that this method could be used for analysis of the specific aromatic amines in industrial products.

Conclusion

This paper has focused on an explanation of test methods for chemical substances contained in manufactured products and measurements of REACH substances of high concern. It is predicted that there will

be an expansion of the regulation of chemical substances in all countries in the future, and chemical analysis can be said to play an important role in getting a grasp on the chemical substance content in manufactured products. In addition, it will be necessary to rapidly obtain information on chemical substance regulations in countries throughout the world and to develop measurement methods.

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