

Analysis Method of Level 1 Prohibited Substances

1. Brief Description of the Analysis Method of Level 1 Prohibited Substances

An example of brief description of the analysis method (high-precision analysis method) for Level 1 Prohibited Substances is the table below.

Target Substance	Analysis Method	Remarks
PCB (Polybiphenyl chloride)	Dissolution → extraction → HRGCMS, GCMS, GC	
PCT (Polyterphenyl chloride)	Dissolution → extraction → GCMS	
Asbestos	Crushing → XRD	
Specified organic tin compound	Dissolution → extraction → derivative → GCMS	
Paraffin chloride	Dissolution → extraction → column cleanup → GCMS	
Specified brominated flame-retardants (PBB, PBDE)	Dissolution → extraction → HRGCMS	
Azo dye and pigment forming specified amines	Specified test. Dissolution → extraction → derivative → GCMS	See 2. IV
Short-chain paraffin chloride (C10-13)	Dissolution → extraction → HRGCMS	
Cadmium and its compounds	Decomposition → ICP-OES or ICP-MS	See 2. I
Lead and its compounds	Decomposition → ICP-OES or ICP-MS	See 2. I
Hexavalent chromium compounds	Dissolution test. Decomposition → diphenylcarbazide method, IC	See 2. III
Mercury and its compounds	Incineration → absorption → reduction/vaporization AAS	See 2. II
Ozone-depleting substances	Volatilization, Desorption → capture GC, GCMS	
Formaldehyde	Volatilization, Desorption → capture → extraction HPLC	See 2. V

HRGCMS: High-resolution gas chromatograph-mass spectrometry
 GCMS: Gas chromatograph mass-spectrometry
 ICP-OES: High-frequency induction-coupling plasma-emission spectroscope
 ICP-MS: High-frequency induction-coupling plasma-mass spectroscope
 GC: Gas chromatography
 HPLC: High-performance liquid chromatography
 IC: Ion chromatography
 XRD: X-ray diffraction
 AAS: Atomic absorption spectrometry

2. Detailed Analysis Method for Level 1 Prohibited Substances

An analysis method for substances ranked as Level 1 Prohibited Substances is introduced below.

The fluorescence X-ray analysis method is shown for lead, cadmium, mercury, and chromium as a screening analysis; for hexavalent chromium, warm-water extracted diphenylcarbazide absorption photometric method as a simple analysis method (Matsushita method). In addition, a high-precision analysis method is introduced for lead, cadmium, mercury, hexavalent chromium, azo compounds, and formaldehyde, etc.

I. Lead, Cadmium, and their Compounds

(1) Screening Analysis

Fluorescence X-ray analysis

A sample with a predetermined volume and weight can be created with relatively simple preparations, including sample cutting, crushing, etc. The presence and concentration of lead and cadmium can be determined promptly by using an analyzer. This method is suited for analyzing plastics, rubber, metal, glass, ceramics, etc. Concentrations can be determined by using the built-in semi-quantitative analysis software (fundamental parameter method) and quantitative analysis software (analytical curve method).

<Analyzer>

Energy-dispersion type fluorescence X-ray analyzer (EDX), Wavelength-dispersion type fluorescence X-ray analyzer (WDX)

(2) High-precision Analysis (Determining the correct quantity of contents)

Preprocessing of a sample involves wet decomposition (including pressure decomposition) under the influence of nitric acid, hydrochloric acid, hydrofluoric acid, hydrogen peroxide acid, etc., incineration under the influence of sulfuric acid or low-temperature incineration with oxygen plasma for preparing a specimen solution. Any precipitation, if generated, is re-dissolved by fluoric acid decomposition or alkaline dissolution decomposition before using it for analysis. The prepared solution specimen is then supplied to an ICP emission spectroscope and the concentration of lead and cadmium in the specimen solution is measured by using the analytical curve produced with the standard solution. The measured concentration values are then converted to lead and cadmium content in a solid sample. As a preprocessing method, it is also possible to use the method described in the first draft¹ of IEC62321.

<Analyzer>

As a rule, ICP optical emission spectroscope (ICP-OES) should be used, but if a similar or better performance is warranted, ICP mass spectroscope (ICP-MS) or atomic absorption spectrometry (AAS) may also be used.

(3) Methods to Analyze Lead in Electroless Nickel Plating

1) Preparation of a lead analysis sample (plated film)

- i) Prepare a thin piece of SUS304 plate as a base material.
- ii) Measure the weight of the SUS304 plate.
- iii) Apply nickel plating to the SUS304 plate in a nickel-plating bath under standard conditions.
- iv) Measure the weight of the plated SUS304 plate.
- v) Calculate the weight of the nickel-plated film from the weight difference before and after plating.

2) Quantitative analysis method of the lead contained in a nickel-plated film

- i) Apply selective thermal dissolution to the nickel-plated film of the plated sample of the above 1) iv) by using an appropriate quantity of (1 + 1) nitric acid.
- ii) Analyze the lead in the solution (test solution) by using either atomic absorption spectrometry, ICP emission spectroscope analysis, and ICP mass spectroscope.

Analyze the lead contained in the dissolved solution (test liquid) by using the atomic absorption spectrometry or ICP optical emission spectroscopy and ICP mass spectrometer.

- iii) If the weight of the nickel-plated film cannot be obtained in the above 1) v) procedure, analyze the nickel in the test solution by using either atomic absorption spectrometry or ICP emission spectroscopy analysis.

Note that optimized analysis conditions need to be determined if the ICP emission spectroscopy analysis is used.

(4) High-precision Analysis of Lead Contained in a Tin-plated Film

(The details of the method are generally not specified, but a temporary method is shown below.)

1) The tin-plated structure to which this method is applicable

Tin-plating + Copper plating (Due to the fact that phosphor bronze used as a base film for copper plating sometimes contains tin and lead, caution is required to prevent dissolved lead from the base layer affecting the measured quantity of lead, depending on the etching method.)

2) Method

When analyzing the lead in a tin-plated film, preprocessing is necessary to prevent dissolution of the lead contained in the base layer of the tin plating.

i) Preparation of etching solution (HCl : HNO₃ : H₂O = 9 : 1 : 10, refer to JIS Z3910: Solder Analysis Method)

ii) Etching the tin-plated film (Heated, and until the copper base layer is visible)

iii) Measure the volume of the etching solution, determine the quantity of tin and lead using ICP emission spectroscopy, and calculate the proportion of lead contained in the tin-plated film.

II. Mercury and its Compounds

(1) Screening Analysis

Fluorescence X-ray analysis

A sample with a predetermined volume and weight can be created with relatively simple preparations, including sample cutting, crushing, etc. The presence and concentration of mercury can be determined promptly by using an analyzer.

This method is suited for analyzing plastics, rubber, metal, glass, ceramics, etc.

Concentrations can be determined by using the built-in semi-quantitative analysis software (fundamental parameter method) and quantitative analysis software (analytical curve method).

<Analyzer>

Energy-dispersion type fluorescence X-ray analyzer (EDX), Wavelength-dispersion type fluorescence X-ray analyzer (WDX)

(2) High-precision Analysis (Determining the correct quantity of contents)

By using pressure decomposition or a decomposition flask with a reflux-cooling device, a sample can be decomposed with sulfuric acid or nitric acid while preventing the volatilization of mercury. The dissolved sample is then analyzed with a reducing-vapor atomic absorption spectrometry or reducing-vapor ICP optical emission spectroscopy. The measured concentration of mercury in the solution is determined with the analytical curve produced with the standard solution and then converted to a solid quantity in the sample. As a preprocessing method, it is also possible to use the method described in the first draft¹ of IEC62321.

<Analyzer>

The use of a reducing-vapor atomic absorption spectrometry (AAS) or reducing-vapor ICP optical emission spectroscopy (ICP-OES) is considered standard but an ICP

mass-spectroscopy (ICP-MS), cold-vapor atomic absorption spectrometry (CVAAS) may also be used if a similar or better performance is expected.

III. Hexavalent Chromium Compounds

Analysis methods for detecting hexavalent chromium compounds in a sample include the X-ray diffraction method or X-ray optical emission spectroscopy. However, these methods cannot determine the concentration. Therefore, the following fluorescence X-ray spectroscopy is used for determining the chromium content first and then the possible inclusion of hexavalent chromium.

(1) Screening analysis

Fluorescence X-ray analysis

A sample with a predetermined volume and weight can be created with relatively simple preparations, including sample cutting, crushing, etc. The presence and concentration of chromium can be determined promptly by using an analyzer. This method is suited for analyzing plastics, rubber, metal, glass, ceramics, etc. However, this method is not suitable for analyzing hexavalent chromium in the surface treatment of metallic objects.

Concentrations can be determined by using the built-in semi-quantitative analysis software (fundamental parameter method) and quantitative analysis software (analytical curve method). This method is not used for measuring hexavalent chromium but for measuring chromium.

<Analyzer>

Energy-dispersion type fluorescence X-ray analyzer (EDX), Wavelength-dispersion type fluorescence X-ray analyzer (WDX)

(2) Simple Analysis Method (Use this method for controlling hexavalent chromium in a chromate processed component/material. Use of the spot-test method described in the first draft of IEC62321^{*1} and the boiling-water extraction method is not permitted.)

Warm-water-extracted diphenylcarbazide absorption spectroscopy

As part of preprocessing, prepare test liquid by extracting the sample in warm water at 80°C for 10 min.

Add the pack test chemical for hexavalent chromium (Kyoritsu Chemical-Check Lab) to the test liquid. Measure absorption near the wavelength 540 nm by using a spectrophotometer (water analysis pack included) and obtain the concentration of hexavalent chromium in the test liquid. By using the hexavalent chromium concentration, the extracted liquid quantity, the surface areas of sample, and the quantity of zinc-plating, convert to the hexavalent chromium quantity per zinc-plating quantity.

<Analyzer>

Shimazu Ultraviolet Visual Ray Photospectrometer UV-mini 1240 (water analysis pack included), Kyoritsu Chemical-Check Lab hexavalent chromium digital pack test

(3) High-precision analysis

Boiling-water-extracted diphenylcarbazide absorption spectroscopy (Used for surface treatment items such as plating, conversion treatments, etc.)

A sample solution is prepared by extracting the content from a solid sample in boiling water. The prepared sample solution is used in diphenylcarbazide absorption spectroscopy or ion-chromatography for selectively determining the concentration of hexavalent chromium.

The concentration of hexavalent chromium in the sample solution is determined using the analytical curve produced from the standard solution and then converted to the quantity of hexavalent chromium (Cr^{6+}) as μg per uniform material mass (g). For a chromate-processed sample, the conversion is made to the quantity of hexavalent chromium (Cr^{6+}) as μg per zinc-plating quantity (Zn) (g) in the plated sample.

JIS/H/8625 (Hexavalent chromium residue quantity measurement) is considered a reference analysis method.

Alkaline-extracted diphenylcarbazide absorption spectroscopy (Used for resin, paint, ink, pigment, etc.)

Heat and extract a crushed sample in alkaline solution, then selectively measure hexavalent chromium by using the diphenylcarbazide absorption spectroscopy. (EPA3060A method)

<Analyzer>

Absorption spectroscope, ion-chromatograph analyzer

IV. Azo Dye and Pigment Forming Specific Amines

The method of decomposing azo compounds and extracting is described in the following references.

LMBG 82.02.2: Analysis of commodities-Detection of particular azo dyes used in textile commodities, LMBG 82.02.3: Analysis of commodities-Detection of particular azo dyes used in leather, and LMBG 82.02.4: Analysis of commodities-Detection of particular azo dyes used in polyester fibers. Specifically, the content is extracted in solvent, sodium thiosulfate is added as a reducing agent, and the decomposed content is re-extracted in solvent. The extracted solution is then measured with a gas chromatograph mass analyzer, liquid chromatograph mass analyzer, or a high-speed liquid chromatograph to determine the content of the specified amines.

Since the above-mentioned test/analysis requires significant cost and time due to the procedure for decomposing and measuring the azo compound, it is recommended that information be obtained from the manufacturer or association that handles the pigment or dye after confirming the relevant color base (C. I. Pigment).

According to the test results by ETAD (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers), the azo-based pigments and dyes shown below are said to clear the daily goods regulation as stipulated in Germany's amine regulations (Fifth revision of the ordinance). Therefore, the following azo-based pigments and dyes do not correspond to Level 1 Prohibited Substances.

C. I. Name	C. I. No .	CAS No .	Regulatory Status
Pigment Yellow 12	21090	6358-85-6	A
Pigment Yellow 13	21100	5102-83-0	A
Pigment Yellow 14	21095	5468-75-7	A
Pigment Yellow 14	-	7621-06-9	A
Pigment Yellow 17	21105	4531-49-1	A
Pigment Yellow 55	21096	6358-37-8	A
Pigment Yellow 83	21108	5567-15-7	A
Pigment Yellow 126	21101	90268-23-8	A
Pigment Yellow 127	21102	68610-86-6	A
Pigment Yellow 174	21098	78952-72-4	A
Pigment Yellow 176	21103	90268-24-9	A
Pigment Orange 13	21110	3520-72-7	A
Pigment Orange 16	21160	6505-28-8	A
Pigment Orange 34 Pigment Orange 35 Pigment Orange 37	21115	15793-73-4	A

C. I.: Color index of pigments and dyes published in the U.K.
Regulatory Status = A: Exempted under the 5th Amendment

V. Formaldehyde

The method of measuring the quantity of formaldehyde released from materials includes the Chamber Method EN717-1 (Wood based panels; determination of formaldehyde release; formaldehyde emission by the chamber method) (Corresponding to 0.1 ppm regulation in Germany's ChemG).

In Japan, a formaldehyde test/analysis method has been determined by JIS A1460, 2001. (Test method for formaldehyde emission from construction boards: Desiccator method) (JIS F****class: 0.3 mg/L or less)

Denmark's formalin regulations specify a chamber method (0.15 mg/m) and a perforator method (25 mg/100 g) as defined by EN 120 (Wood based panels; determination of formaldehyde content; extraction method called perforator method; German version EN 120: 1992).

VI. Packaging Materials

The quantity of cadmium, lead, mercury, and hexavalent chromium in packaging materials such as paper, plastics, ink, etc. should not exceed 100 ppm in total. In addition, the cadmium content in plastic materials must be 75 ppm or less.

In principle, the analysis of these four elements shall be made using the preparation and analysis methods mentioned in I, II, and III above. However, as far as hexavalent chromium is concerned, when the solution decomposed with nitric acid, sulfuric acid or hydrogen peroxide and analyzed by atomic absorption spectrometry, ICP optical emission spectroscopy, or ICP mass spectroscopy guarantee that the total chromium content be 2 ppm or less, then the analysis of hexavalent chromium inclusion by means of a solution test may be omitted.

VII. PBB, PBDE in Resin

<Preprocessing>

After crushing a sample, use an organic solvent suited for resolving samples such as toluene or tetrahydrofuran, combined with an appropriate extraction method such as the Soxhlet method to swell and extract PBB, PBDE. In order to remove the resin content in the solution, apply a cleanup process such as re-sedimentation in poor solvent, centrifugal separation, silica gel absorption, etc. As a preprocessing method, it is also possible to use the method described in the first draft¹ of IEC62321.

<Measurement method>

Introduce the conditioned sample solution into the Quadruple GC-MS (gas chromatograph mass spectrometer) and compare with the retention time, mass pattern and spectrum intensity of a known standard sample to perform qualitative and quantitative analysis.

<Analyzer>

Use a quadruple gas chromatograph mass spectrometer (GC-MS) and a magnetic high-resolution mass spectrometer (GC-HRMS). For the standard sample, use PBB composite (mixture of multiple types of brominated biphenyls), PBDE composite (mixture of multiple types of brominated diphenyl-ethers) and a single substance (at least 5 types of standard samples, 4 to 10-brominated substances, 10-brominated diphenyl ethers is essential).

*1: The first draft of IEC62321 (English, Japanese) is obtainable from the website of the Japanese Standards Association using "IEC Search".

URL: <http://www.jsa.or.jp/>

Revision History

Location	Revised Content
Chapter 2	Deleted Since the specified substances are contained in a variety of forms, there exists no single universal analysis method effective for most substances.
Chapter 2 I. 2), II. 2), VII	Added As a preprocessing method, it is also possible to use the method described in the first draft ^{*1} of IEC62321.
Chapter 2 I. 2)	Deleted An alternate method is to use a solid sample for frameless atomic absorption spectrometry (FLAAS), a method capable of a quantitative analysis.
Chapter 2 I. 4)	Added High-precision Analysis of Lead Contained in a Tin-plated Film
Chapter 2 III. 1)	Added However, this method is not suitable for analyzing hexavalent chromium in the surface treatment of metallic objects.
Chapter 2 III. 2)	Added Use of the spot-test method described in the first draft of IEC62321 ^{*1} and the boiling-water extraction method is not permitted.
Chapter 2 III. 3)	Deleted Alternately, the sample is extracted in an alkaline solution and diluted to a known volume with ion-exchanged water.
Chapter 2 III. 3)	Added Converted to the quantity of hexavalent chromium (Cr ⁶⁺) as µg per uniform material mass (g).
Ending	Added *1 The first draft of IEC62321 (English, Japanese) is obtainable from the website of the Japanese Standards Association using "IEC Search". URL: http://www.jsa.or.jp/