

RICOH

**RICOH GROUP
Green Procurement
Standards**

Annex

**Environmentally Sensitive Chemical Substances
Analysis Guide**

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RICOH Co., Ltd./ RICOH GROUP

Table of Contents

1. Preface	P.02
2. Problematic cases.....	P.02
2-1. Case 1	
2-2. Case 2	
2-3. Case 3	
2-4. Case 4	
3. Target range for analysis.....	P.03
4. Analytical system table	P.04
5. General methods for analyses	P.05
5-1. Analysis of Cd, Pb, Hg, T-Cr(Cr's), T-Br(Br's)	
5-1-1. Metal samples	
5-1-1-1. Normal analysis: Analysis by X-ray fluorescence	P.05
5-1-1-2. Detailed analysis: Analysis by ICP	P.06
5-1-2. Plastic samples	
5-1-2-1. Normal analysis: Analysis by X-ray fluorescence	P.07
5-1-2-2. Detailed analysis: Analysis by ICP	P.08
5-1-3. Ceramic samples.	
5-1-3-1. Normal analysis: Analysis by X-ray fluorescence	P.09
5-1-3-2. Detailed analysis: Analysis by ICP	P.10
5-1-4. Plating/ other thin layer samples	
5-1-4-1. Normal analysis: Analysis by X-ray fluorescence	P.11
5-1-4-2. Detailed analysis: Analysis by ICP	P.12
5-2. Cr() Analysis	
5-2-1. Chromate samples (without coated layer)	
5-2-1-1. Normal analysis: Analysis by diphenylcarbazide	P.13
5-3. PBB / PBDE Analysis	
5-3-1. Plastic samples	
5-3-1-1. Normal analysis: Analysis by GC-MS	
.....	P.14
6. Special analytical method (important).....	P.15
6-1. Pb Analysis	
6-1-1. Micro-metal (including thin layer) samples [Example: solders/ plating of IC lead parts, etc.]	
6-1-1-1.	
Initial detailed analysis: Analysis by LA-ICP-MS.....	P.15
6-1-1-2. Management (analysis).....	P.15
6-2. Cr() Analysis	
6-2-1. Chromate samples	
6-2-1-1. Initial detailed analysis: analysis by diphenylcarbazide (after polish and extraction).....	P.16
6-2-1-2. Management (analysis).....	P.17

1. Preface

RICOH GROUP, by the announcement of RICOH GROUP Green Procurement Standards, has been asking all companies concerned to deliver products, parts and materials which meet these Standards.

This time around, in order to further enhance the certainty of compliance, RICOH GROUP has prepared an Annex to the Sixth Edition of Green Procurement Standards as a separate volume, which describes the details of analytical methods for substances. This volume covers particularly those addressed in RoHS only among all banned substances described in the Sixth Edition.

The companies concerned are requested to compare the problematic cases described in the following pages of this volume as a reference to the conditions in the cases of your companies, and if you find any problem, calculate correct analytical values by following the analytical methods described in the following, and implement correct management of environmentally sensitive substances.

Furthermore, even when you find no problem in particular, RICOH GROUP requests all companies concerned to understand the descriptions in this volume and make use of them as reference materials for analyses in the future. However, RICOH GROUP does not deny any other method of which precision is of equal accuracy or better when compared to the analytical methods described in these standards.

2. Problematic cases

2-1. Case 1

The soldering facility was used for both eutectic soldering line and Pb-free soldering line. Due to contamination which occurred during switch over between eutectic solders and Pb-free solders, Pb concentration in the solders exceeded the standard value in more than one places. However, because the result of external analysis showed the Pb content to be less than the standard value, the products were evaluated as acceptable. In this case, the external company that conducted analysis was asked to simply measure the content rate, the external company that conducted analysis used the total weight of the sample requested for analysis for calculating the Pb concentration value instead of measuring the Pb content rate of each soldered part. As a result, the Pb content rate appeared incommensurably less than the actual values, and thus, the rate was reported to be less than the standard value.

Countermeasure: Conduct analysis by taking scope of analysis into account, or specify scope of analysis in case of outsourcing analyses (Reference: Section 5, 6)

2-2. Case 2

Although it was known that chromate process was applied, since absolutely no Cr() was detected as a result of the analysis conducted by an analysis company, it was mistakenly judged that trivalent chromate process was used, when in reality, hexavalent chromate process was used. In this case, Cr() was not extracted at all because the analysis company conducted a routine analysis without checking if coating was applied on the chromate layer, when in reality coating was indeed applied on the chromate layer. (Many analysis companies conduct analysis without taking film into account unless the companies which outsource the analysis to them specifically request to check the film as in this case.)

Countermeasure: When no Cr() is detected even though chromate process was applied, the existence of a film must be suspected in conducting analyses. (Reference: Section 6-2-1-1)

2-3. Case 3

Since the Pb contents of Sn balls, which were added to the solder bath, were about 100ppm, it was assumed that the Pb in the said solder bath would not exceed 1000ppm semi-permanently. In this case, there was elution of Pb from other parts, and consequently Pb content in the solder bath was more than 1000ppm.

Countermeasure: Assuming some change occurs in the material, conduct analysis periodically. (Reference: Sections 5-1-1 and 6-1-1)

2-4. Case 4

It was judged alright because the Pb concentration of the plating liquid was less than several ppm. In this case, Pb concentration of the plated layer of the product was thickened to exceed the Pb concentration of the plating liquid. As a result, subsequent Pb content exceeded 1000ppm. (Pb concentration of a lated layer may be thickened by more than several hundred times.)

Countermeasure: Conduct analysis of actual object even when the analysis of the actual object is difficult. (Reference: Sections 5 and 6-1-1)

3. Scope of target of analysis

When determining the content rate of a substance by analysis, depending on what is chosen as the population parameter (scope of target of analysis), not only the analyzed value but also the volume of samples to be analyzed will change, which greatly influences methods to be adopted for analysis. Since it is likely that misunderstanding occurs with respect to these points, scopes of target of analyses ,from which analyzed values are produced, are described in the following.

- (i) When there is a material of which continuity is blocked by another material:

The domain in which this material exists is regarded as an independent target range for analysis, excluding (ii) in the following.

(Example: Each leg of IC is regarded as a target range for analysis independently.)

- (ii) When there is (are) a layer (layers) of less than 1 μ m thick which is (are) comprised of material(s) different from those of other layers.

Considering that a material layer of less than 1 μ m thick is normally inseparable, the surface layer (layers) of less than 1 μ m thick is (are) collectively regarded as one target range for analysis combined with another inner layer of more than 1 μ m thick located adjacent to a layer of less than 1 μ m thick inside.

However, the following must be taken into consideration.

- When there is a layer of less than 1 μ m thick directly on top of a layer of more than 200 μ m thick, the 200 μ m thick point at maximum of the

layer of more than 200 μ m thick is set for combining with a layer or layers of less than 200 μ m thick as one target range for analysis.

- When there is an unknown layer of less than 1 μ m thick which is sandwiched between two layers of more than 1 μ m thick, the thinner layer must be chosen to be combined with the inside layer

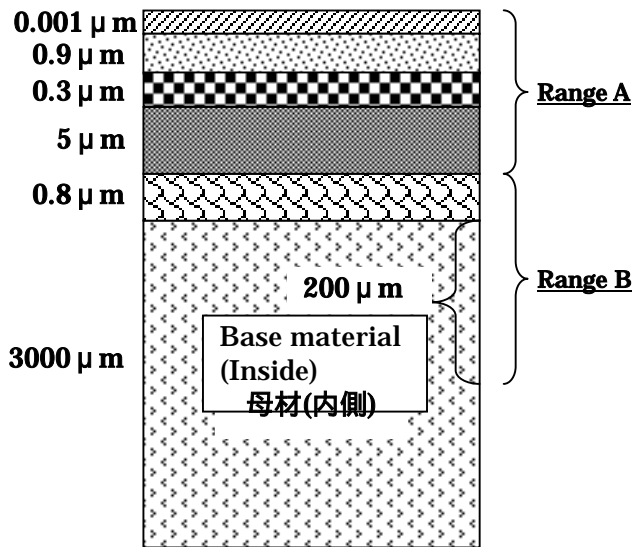


Fig.1 Concept of target range for

Explanation for layered structures

(1) Range A

All four layers on the surface comprise target range for analysis, because all of the three layers on the surface are less than 1 μ m thick respectively.

(2) Range B

Since the fifth layer is less than 1 μ m thick, the target range for analysis includes up to 200 μ m deep inside from the surface of the base material which is 3000 μ m thick.

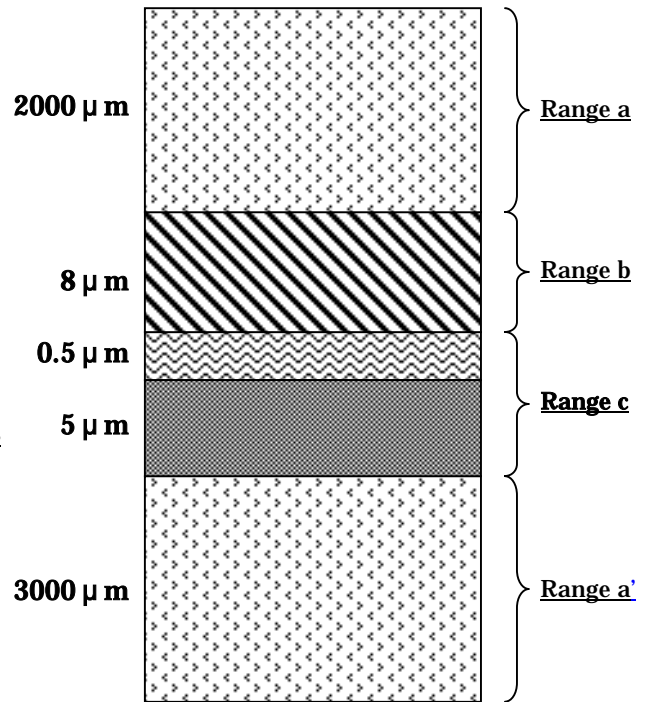


Fig.2 Concept of target range for analysis of

Explanation for sandwiched layered structure (of which inside is unknown)

(1) Range a a' b

Each layer becomes a target for analysis independently because each layer is more than 1 μ m thick.

(2) Range c

The layer in the center which is 0.5 μ thick is not regarded as a target range for analysis by itself because it is less than 1 μ thick. Here, since the 0.5 μ thick layer is sandwiched in between layers of 8 μ thick and 5 μ thick respectively, combination of the two layers of 0.5 μ thick and the 5 μ, which is thinner (than 8 μ) comprises the target range for analysis.

4. Analytical system table

Characteristics of substance	Analyzer	Banned substance				
		Cd	Pb	Hg	Cr()	PBB/PBDE
Metal	X-ray fluorescence instrument	5-1-1-1 (Note: Analysis of Hg may not be necessary)			-	-
	ICP-AES ICP-MS and AAS(excluding Hg) CV-AAS(Hg only)	5-1-1-2 <i>(Note: Analysis of Hg may not be necessary)</i>			-	-
Plastic	X-ray fluorescence instrument	(Note: Evaluation of Cr() is conducted with T-Cr, and that of PBB/PBDE with T-Br.				
	ICP-AES ICP-MS and AAS(excluding Hg) CV-AAS(Hg only)	5-1-2-2 (Note: Evaluation of Cr() is conducted with T-Cr)				Disapprove
	GC-MS (HR)GC-(HR)MS and IAMS	Disapprove	Disapprove	Disapprove	Disapprove	5-3-1-1
Ceramic	X-ray fluorescence instrument	5-1-3-1 (Note: Evaluation of Cr() is conducted with T-Cr)				-
	ICP-AES ICP-MS and AAS(excluding Hg) CV-AAS(Hg only)	5-1-3-2 (Note: Evaluation of Cr() is conducted with T-Cr)				-
Plated thin layer	X-ray fluorescence instrument	5-1-4-1 (Note: Evaluation of Cr() is conducted with T-Cr)				-
	ICP-AES ICP-MS and AAS(excluding Hg) CV-AAS(Hg only)	5-1-4-2 (Note: Evaluation of Cr() is conducted with T-Cr)				-
	Diphenylcarbazine absorption photometer (General pretreatment) and IC	Disapprove	Disapprove	Disapprove	5-2-1-1	Disapprove
	Diphenylcarbazine absorption photometer (Special pretreatment)	Disapprove	Disapprove	Disapprove	6-2-1-1	Disapprove
	Ion test paper	Disapprove	Disapprove	Disapprove	6-2-1-2	Disapprove
	LA-ICP-MS	Approve	6-1-1-1	Approve	Approve Evaluation by T-Cr	-
Micro-metal	LA-ICP-MS	Approve	6-1-1-1	Approve	Approve Evaluation by T-Cr	-

Note: **Italic bold letters** indicate high precision analysis / “and” means it is not described in this Guides / “ - ” indicates it is excluded from the target of analysis

Reference: Abbreviation of apparatus for analysis

ICP-MS	: Inductively-coupled plasma mass spectrometer
ICP-AES	: Inductively-coupled plasma emission spectrometer
AAS	: Atomic absorption spectrometer
IC	: Ion chromatography
CV-AAS	: Reduction vaporization atomic absorption spectrometer
GC-MS	: Gas chromatograph mass spectrometer
(HR)GC-(HR)MS	:(High resolution) Gas chromatograph (high resolution) mass spectrometer
IAMS	: Ion attachment mass spectrometer
LA-ICP-MS	:Laser absorption inductively-coupled plasma mass spectrometer

5. General methods of analysis

These general methods of analysis assume cases in which uniform and sufficient quantity of samples can be secured. Normally, sample collected from one place must be analyzed as much as possible. (Although it is not recommended, when the content rate of material to be measured is apparently the same in more than one places, it is possible to conduct analysis by regarding all of the samples collected from more than one place as one target range for analysis.)

As for the method of analysis, basically, see the latest version of International Standard IEC-62321 (method of analysis compatible with RoHS). The available version as of February 2008 is CDV of Ed.1.0 : 2006 (published by Japanese Standards Association)

5. General methods of analyses	
5-1. Analysis of Cd, Pb, Hg, T-Cr(all Cr's), T-Br(all Br's)	
5-1-1. Metal samples	
<ul style="list-style-type: none"> • Analysis of T-Cr is not necessary. (Example: stainless steel) • Analysis of T-Br is not necessary (flame retardant does not exist in flame retardant) 	
5-1-1-1. Normal analysis: Analysis by X-ray fluorescence	
Preparation	Standard sample <ul style="list-style-type: none"> • Commercially supplied sample (similar material) Or, <ul style="list-style-type: none"> • Sample (similar material) of which value is specified by other high precision analysis
	Time for sample analysis <ul style="list-style-type: none"> • Time must be set so that the peak value of the aforementioned standard sample in the neighborhood of its threshold value can be confirmed.
	Analytical curve <ul style="list-style-type: none"> • Prepare analytical curve by sample analysis and time analysis of the aforementioned standard sample
Measurement	Placement of sample <ul style="list-style-type: none"> • Place a sample so that the target of an analyzer is covered completely by the target area of measurement of the sample.

	<p>Analysis</p> <ul style="list-style-type: none"> • Implement quantitative analysis by analytical curve (When the composition of the sample of which quantitative analysis is prepared is different from that of the sample to be measured, it must be corrected separately)
Notes	<p>When the monitor to confirm target is installed in a different angle from that of X-ray irradiation, it must be confirmed that the sample's target area for measurement, especially the orientation of height, is in line with the prescribed location.</p>
	<p>In case of dealing with thin samples, confirm that the signal volume does not change when the sample is made thick. (In a case when X-ray source is 50keV, X-ray easily transmits Al alloy. (In the case of Sn alloy, 100 μ m is sufficient)</p>
	<p>When implementing analysis, take into consideration a blocking element which shows a peak in the same analytical location in the spectrum</p>

5. General methods of analysis	
5-1. Analysis of Cd, Pb, Hg, T-Cr(All Cr's), T-Br(All Br's)	
5-1-1. Metal sample	
<ul style="list-style-type: none"> • Analysis of T-Cr is not necessary (Example: stainless steel) • Analysis of T-Br is not necessary (flame retardant does not exist in metal) 	
5-1-1-2. Detailed analysis: Analysis by ICP	
<ul style="list-style-type: none"> • Apply to ICP-AES(ICP emission analysis) and ICP-MS(ICP mass analysis) • Analyze solution in which sample is dissolved 	
Preparation	Standard sample <ul style="list-style-type: none"> • Reagent maker's standard (mixed) reagent
	Pretreatment of sample for analysis <ul style="list-style-type: none"> • Normally, heat sample by acid other than sulfuric acid for dissolution (banned substance may disappear by evaporation depending on the selection of acid and heating temperature.) • Completely dissolve sample by "analytical form which is compatible with RoHS" (not to leave any residue/precipitate). • Adjust concentration to prepare sample for analysis
	Analytical curve <ul style="list-style-type: none"> • Prepare analytical curve by mixing/ diluting standard solution (including standard solution of internal standard element candidate)
Measurement	Stabilization <ul style="list-style-type: none"> • Expose ICP to warm air. • Confirm the background is low enough (Introduce high purity low concentration nitric acid solution into ICP) • Check appropriate detection range is activated by using standard solution.
	Analysis <ul style="list-style-type: none"> • Sample for analysis which is diluted to the concentration level where analytical curve can be used must be analyzed once • Add to sample for analysis standard solution as an internal standard which includes an element which is hardly present as a constituent element • Introduce sample for ICP analysis to which internal standard is added into ICP for quantification (Confirm that precipitate does not form due to reduction in acid concentration) • When residue/ precipitate is formed when sample is dissolved, use analytical form without destruction (Example: X-ray fluorescence instrument), and if banned substance is included in it, dissolve with other chemical and analyze
Notes	Since ICP is very sensitive, it is recommended to wash containers used for preparation of resolution with nitric acid in advance, and use ultra-pure water for all water to be used.

5. General methods of analysis	
5-1. Analysis of Cd, Pb, Hg, T-Cr(All Cr's), T-Br(All Br's)	
5-1-2. Plastic sample	
<ul style="list-style-type: none"> When T-Cr exceeds the threshold, go back to the added raw material, and specify its Cr() content rate. 	
5-1-2-1. Normal analysis: Analysis by X-ray fluorescence	
Preparation	Standard sample <ul style="list-style-type: none"> Commercially supplied sample (similar material) Or, <ul style="list-style-type: none"> Sample (similar material) of which value is specified by other high precision analysis
	Time for sample analysis <ul style="list-style-type: none"> Time must be set so that the peak value of the aforementioned standard sample in the neighborhood of its threshold value can be confirmed.
	Analytical curve <ul style="list-style-type: none"> Sample analysis and time analysis of the aforementioned standard sample Prepare analytical curve by internal standard method in which division by background adjacent to a signal is applied
Measurement	Placement of sample <ul style="list-style-type: none"> Place a sample so that the target of an analyzer is covered completely by the target area of measurement of the sample.
	Analysis <ul style="list-style-type: none"> Implement quantitative analysis by analytical curve (When the composition of the sample of which quantitative analysis is prepared is different from that of the sample to be measured, it must be corrected separately)
Notes	When the monitor to confirm target is installed in a different angle from that of X-ray irradiation, it must be confirmed that the sample's target area for measurement, especially the orientation of height, is in line with the prescribed location.
	Since X-ray transmits ordinary plastic, do not place any objects not to mention plastic/ metals within the range of measurement to prevent unnecessary signal from coming back. (Extremely-thin film is acceptable)
	Constituent element of sample must be taken into consideration when conducting analysis because background may increase or peak may be produced in the same location of analysis, which cause obstruction, depending on the constituent element of sample

5. General methods of analysis	
5-1. Analysis of Cd, Pb, Hg, T-Cr(All Cr's), T-Br(All Br's)	
5-1-2. Plastic sample	
<ul style="list-style-type: none"> When T-Cr exceeds the threshold, go back to the added raw material, and specify its Cr() content rate. 	
5-1-2-2. Detailed analysis: Analysis by ICP	
<ul style="list-style-type: none"> Apply to ICP-AES(ICP emission analysis)and ICP-MS(ICP mass spectrography) Analyze resolution in which sample is dissolved (teflon is not approved). 	
Preparation	Standard sample <ul style="list-style-type: none"> Reagent maker's standard (mixed) reagent
	Pretreatment of sample used for analysis <ul style="list-style-type: none"> Normally, samples are heated by acids other than sulfuric acid for dissolution (banned substance may disappear by evaporation depending on the selection of acid and heating temperature.) Adjust concentration to prepare sample for analysis
	Analytical curve <ul style="list-style-type: none"> Prepare analytical curve by mixing/ diluting standard solution (including standard solution of internal standard element candidate)
Measurement	Stabilization <ul style="list-style-type: none"> Expose ICP to warm air. Confirm the background is low enough (Introduce high purity low concentration nitric acid solution into ICP) Check appropriate detection range is activated by using standard solution.
	Analysis <ul style="list-style-type: none"> Sample for analysis which is diluted to the concentration level where analytical curve can be used must be analyzed once Add to sample for analysis standard solution as an internal standard which includes an element which is hardly present as a constituent element Introduce sample for ICP analysis to which internal standard is added into ICP for quantification (Confirm that precipitate does not form due to reduction in acid concentration) When residue/ precipitate is formed when sample is dissolved, use analytical form without destruction (Example: X-ray fluorescence instrument), and if banned substance is included in it, dissolve with other chemical and analyze
Notes	Since ICP is very sensitive, it is recommended to wash containers used for preparation of resolution with nitric acid in advance, and use ultra-pure water for all water to be used.

5. General methods of analysis	
5-1. Analysis of Cd, Pb, Hg, T-Cr (all Cr's), T-Br (all Br's)	
5-1-3. Ceramic sample	
5-1-3-1. Normal analysis: Analysis by X-ray fluorescence	
Preparation	Standard sample <ul style="list-style-type: none"> • Commercially supplied sample (similar material)
	Or, <ul style="list-style-type: none"> • Sample (similar material) of which value is specified by other high precision analysis
	Time for sample analysis <ul style="list-style-type: none"> • Time must be set so that the peak value of the aforementioned standard sample in the neighborhood of its threshold value can be confirmed.
	Analytical curve <ul style="list-style-type: none"> • Prepare analytical curve by sample analysis and time analysis of the aforementioned standard sample
Measurement	Placement of sample <ul style="list-style-type: none"> • Place a sample so that the target of an analyzer is covered completely by the target area of measurement of the sample.
	Analysis <ul style="list-style-type: none"> • Implement quantitative analysis by analytical curve (When the composition of the sample of which quantitative analysis is prepared is different from that of the sample to be measured, it must be corrected separately)
Notes	When the monitor to confirm target is installed in a different angle from that of X-ray irradiation, it must be confirmed that the sample's target area for measurement, especially the orientation of height, is in line with the prescribed location.
	In case of dealing with thin samples, confirm that the signal volume does not change when the sample is made thicker. (In a case when X-ray source is 50keV, the X-ray easily transmits material mainly consisting of Si. (When Fe is the main constituent, 1mm or more is necessary))

5. General methods of analysis	
5-1. Analysis of Cd, Pb, Hg, T-Cr (All Cr's), T-Br (All Br's)	
5-1-3. Ceramic sample	
5-1-3-2. Detailed analysis: Analysis by ICP	
<ul style="list-style-type: none"> • Applied to ICP-AES(ICP emission analysis) and ICP-MS(ICP mass analysis) • Analyze solution in which sample is dissolved 	
Preparation	Standard sample <ul style="list-style-type: none"> • Reagent maker's standard (mixed) reagent
	Pretreatment of sample for analysis <ul style="list-style-type: none"> • Normally, samples are heated by acids other than sulfuric acid using a sealed container (made of Teflon, etc.) which is not corroded by acid. • Adjust concentration to prepare sample for analysis
	Analytical curve <ul style="list-style-type: none"> • Prepare analytical curve by mixing/ diluting standard solution (including standard solution of internal standard element candidate)
Measurement	Stabilization <ul style="list-style-type: none"> • I Expose ICP to warm air. • Confirm the background is low enough (Introduce high purity low concentration nitric acid solution into ICP) • Check appropriate detection range is activated by using standard solution.
	Analysis <ul style="list-style-type: none"> • Sample for analysis which is diluted to the concentration level where analytical curve can be used must be analyzed once • Add to sample for analysis standard solution as an internal standard which includes an element which is hardly present as a constituent element • Introduce sample for ICP analysis to which internal standard is added into ICP for quantification (Confirm that precipitate does not form due to reduction in acid concentration) • When residue/ precipitate is formed when sample is dissolved, use analytical form without destruction (Example: X-ray fluorescence instrument), and if banned substance is included in it, dissolve with other chemical as much as possible and analyze
Notes	Since ICP is very sensitive, it is recommended to wash containers used for preparation of resolution with nitric acid in advance, and use ultra-pure water for all water to be used.

5. General methods of analysis	
5-1. Analysis of Cd, Pb, Hg, T-Cr (All Cr's), T-Br (All Br's)	
5-1-4. Plating/ other thin layer sample	
<ul style="list-style-type: none"> • Separate the target range in large amount with file and collect it for analysis (See target range for analysis in Section 3) 	
5-1-4-1. Normal analysis: Analysis by X-ray fluorescence	
Preparation	Standard sample <ul style="list-style-type: none"> • Commercially supplied sample (similar material) <p>Or,</p> <ul style="list-style-type: none"> • Sample (similar material) of which value is specified by other high precision analysis
	Time for sample analysis <ul style="list-style-type: none"> • Time is set so that the peak value of the aforementioned standard sample in the neighborhood of its threshold value can be confirmed.
	Analytical curve <ul style="list-style-type: none"> • Prepare analytical curve after sample analysis and time analysis of the aforementioned standard sample
	Pre-treatment of sample <ul style="list-style-type: none"> • Use a small-caliber container so that a collected sample increases in thickness rather than in width, especially in the case of light element.
Measurement	Placement of sample <ul style="list-style-type: none"> • Place a sample so that the target of an analyzer is covered completely by the target area of measurement of the sample.
	Analysis <ul style="list-style-type: none"> • Implement quantitative analysis by analytical curve (When the composition of the sample of which quantitative analysis is prepared is different from that of the sample to be measured, it must be corrected separately) • When an element of base material was included in collected sample for measurement, conduct an analysis of base material only after scaling off the plating, etc. and exclude its influence by using the following formula. (Example of calculation shows that of plating) <p>Definition:</p> <p>In sample for measurement, [concentration of target element (A) Concentration of main element of plating (C)]</p> <p>In base material, [concentration of target element (B) Concentration of main element of plating (D) Concentration of main element of plating in plating in theory (E)]</p> <p>[Content rate of target element in plating] $= A \times ((E - D) / (C - D)) - B \times ((E - C) / (C - D))$ (when C = D, caution must be used because error is big in this case)</p>

Notes	When the monitor to confirm target is installed in a different angle from that of X-ray irradiation, it must be confirmed that the sample's target area for measurement, especially the orientation of height, is in line with the prescribed location.
	In case of dealing with thin samples, confirm that the signal volume does not change when the sample is made thicker. (In a case when X-ray source is 50keV, the X-ray easily transmits Al alloy. (In the case of Sn alloy, 100 μ m is sufficient))
	Constituent element of sample must be taken into consideration when conducting analysis because background may increase or peak may be produced in the same location of analysis, which cause obstruction, depending on the constituent element of sample

5. General methods of analysis	
5-1. Analysis of Cd, Pb, Hg, T-Cr(All Cr's), T-Br(All Br's)	
5-1-4. Plating/ other thin layer sample	
<ul style="list-style-type: none"> Separate the target range in large amount with file and collect it for analysis (See target range for analysis in Section 3) 	
5-1-4-2. Detailed analysis: Analysis by ICP	
<ul style="list-style-type: none"> Apply to ICP-AES(ICP emission analysis)and ICP-MS(ICP mass analysis) Analyze solution in which sample is dissolved 	
Preparation	Standard sample <ul style="list-style-type: none"> Reagent maker's standard (mixed) reagent
	Pretreatment of sample for analysis <ul style="list-style-type: none"> Normally, heat sample by acid other than sulfuric acid for dissolution (banned substance may disappear by evaporation depending on the selection of acid and heating temperature.) Completely dissolved by "methods of analysis compatible with RoHS" (not to leave any residue/ precipitate) Adjust concentration to prepare sample for analysis (Although basically, it is more desirable to dissolve sample after mechanically collecting target layer only, separation by chemical process is also acceptable)
	Analytical curve <ul style="list-style-type: none"> Prepare analytical curve by mixing/ diluting standard solution (including standard solution of internal standard element candidate)
Measurement	Stabilization <ul style="list-style-type: none"> Expose ICP to warm air. Confirm the background is low enough (Introduce high purity low concentration nitric acid solution into ICP) Check appropriate detection range is activated by using standard solution.

	<p>Analysis</p> <ul style="list-style-type: none"> • Sample for analysis which is diluted to the concentration level where analytical curve can be used must be analyzed once • Add to sample for analysis standard solution as an internal standard which includes an element which is hardly present as a constituent element • Introduce sample for ICP analysis to which internal standard is added into ICP for quantification (Confirm that precipitate does not form due to reduction in acid concentration) • When residue/ precipitate is formed when sample is dissolved, use analytical form without destruction (Example: X-ray fluorescence instrument), and if banned substance is included in it, dissolve with other chemical and analyze
Notes	<p>Since ICP is very sensitive, it is recommended to wash containers used for preparation of resolution with nitric acid in advance, and use ultra-pure water for all water to be used.</p>

5. General methods of analysis	
5-2. Cr () analysis	
5-2-1. Chromate sample (without coated layer)	
<ul style="list-style-type: none"> • When Cr() chromate treatment liquid is used, and Cr() is not ultimately eliminated, it is regarded as intentional content in terms of RICOH Group's Green Procurement and thus not approved even when Cr() content is 1000ppm or less. • When Cr() is not intentionally contained, sample of plated part of which T-Cr analysis is difficult and sample whose T-Cr is 1000ppm or more, their content rates of Cr() must be identified by chemical analysis. 	
5-2-1-1. Normal analysis: Analysis by diphenylcarbazide	
Preparation	Obtain data for rough calculation of content rate <ul style="list-style-type: none"> • Obtain surface area and average thickness of the layer of target area for analysis (see Section 3) in advance
	Standard sample <ul style="list-style-type: none"> • Reagent maker's standard reagent
	Pretreatment of sample <ul style="list-style-type: none"> • Soak sample in boiling water (pure water) for 10 minutes, and extract Cr() in the chromate layer • Adjust pH by using buffering agent
	Analytical curve <ul style="list-style-type: none"> • Adjust concentration of aforementioned standard sample, adjust its pH, and make it react with diphenylcarbazide to give a color, and then prepare analytical curve of absorbance.
Measurement	Analysis <ul style="list-style-type: none"> • Confirm that appropriate detection range is produced by using standard solution • Divide pH adjusted solution of Cr() extracted from sample into two or more portions, and use one of them as background of measurement, and use another to give a color by adding diphenylcarbazide, and take rough measurement of extracted amount of each portion by using analytical curve with absorptiometer. • Calculate rough content rate of Cr() by using the extracted amount and the surface area and thickness of the layer of target range for analysis.
Notes	This method cannot be used when extraction solution already has dark coloring.
	When a pH value swing over to extreme acidity or alkaline, said data must not be used. (There is a high possibility of change in valence of Cr ())

5. General methods of analysis	
5-3. PBB / PBDE Analysis	
5-3-1. Plastic sample	
• Extraction is difficult depending on type of plastic	
5-3-1-1. Normal analysis: Analysis by GC-MS	
Preparation	Selection of solvent <ul style="list-style-type: none"> • When selecting solvent for extracting PBB/PBDE, select one that dissolve resin content of sample and elute PBB/PBDE as much as possible
	Pretreatment of sample <ul style="list-style-type: none"> • Pulverize sample plastic mechanically • Extract enough sample by using soxhlet extraction method, etc.
Measurement	Analysis <ul style="list-style-type: none"> • Add to extracted solution standard solution as internal standard • Enable monitoring of increase and decrease of target substances, and analyze each bromine substance independently • Analyze T-Br by different instruments, and when its presence is found, re-examine other extraction methods.
Notes	Since PBB and PBDE are photodegradable/ pyrolytic, pay attention to light interception and temperature so that the content will not change before the addition of internal standard.
	When Br is incorporated into the plastic, examination of extracted amount is difficult. In this case, use thermal extraction (thermal desorption) and analyze.

6. Special methods of analysis (Important)

These special methods of analysis are suggested for cases in which “enough sample amount cannot be secured” or “there is an obstruction in conducting analysis”. (Although this is not recommended, but when the content rate of material to be measured is apparently the same in more than one places, it is possible to conduct analysis by regarding all of the samples collected from more than one place as one target range for analysis.)

6. Special method of analysis	
6-1. Analysis of Pb	
6-1-1. Micro-metal (including thin layer) samples [Example: solders/ plating of IC lead parts, etc.]	
<ul style="list-style-type: none"> • Normally, several kinds of plating are applied to electronic parts such as leads. Then the leads are fixed on a substrate by soldering. However, due to small amounts of [plating/ soldering] used, it is often impossible to analysis them in normal cases. Here, analysis/ management methods which can address to such situations are described. 	
6-1-1-1. Initial detailed analysis	
Preparation	Pretreatment of sample <ul style="list-style-type: none"> • When a sample is large, it will make collection of light of laser difficult. Thus, normally, a sample must be broken down into pieces of squares of about 1 cm² be mechanically by a saw or nipper, etc.
Measurement	Analysis <ul style="list-style-type: none"> • Set a sample in a sample room and wait for replacement of air. Then, eradiate it with a laser at 100 μm, and lift airborne matter on an air current, then analyze it by ICP-MS. (At this time, measure the background as well where the laser is not eradiated) • Calculate the content rate of banned substance in the direction of the depth (mainly surface) from the comparison of strength of each constituent element (Example of an institution which is capable of using this method: JFE Techno-Research Corporation)
Notes	Since this method is impacted by segregation, when the value shows more than half of the threshold, break up three parts or more and take samples from them and adopt their average value.
6-1-1-2. Management (analysis)	
<p>It is not realistic to conduct expensive analyses for all of the targets in order to confirm process maintenance. So, first, figure out correlation between LA-ICP-MS and X-ray fluorescence instrument, etc., which enables inexpensive and periodical analysis, and then carry out subsequent process management by using inexpensive analysis equipments. (See the following concerning taking samples).</p> <ul style="list-style-type: none"> • In the case of plating: <ul style="list-style-type: none"> Apply plating to cover enough area for analysis on a dummy substrate, etc. made of the same materials as those of actual samples under the same conditions (same process) as those of actual samples, and then collect samples. • In the case of flow soldering 	

Collect samples directly from the solder bath in the same process

• In the case of paste soldering

Collect samples from both edges (two places on the right and the left) and the center (one place) on the screen in the same process

• In the case of manual soldering

Collect sample from the solder applied in large amount on a normal substrate in the same process.

(Example: In correlation model, when Pb was 800ppm in LA-ICP-MS, whereas it was 50ppm in an analysis by X-ray fluorescence instrument which included base material, if it read 62.5ppm or more in the same fluorescent X-ray analysis conducted for the confirmation of process maintenance, it is a sign of abnormality.)

6. Special methods of analysis	
6-2. Analysis of Cr()	
6-2-1. Chromate Sample (including the case in which coated layer is present)	
<p>• When Cr() chromate treatment liquid is used, and Cr() is not ultimately eliminated, it is regarded as intentional content in terms of RICOH Group's Green Procurement and thus not approved even when Cr() content is 1000ppm or less.</p> <p>When Cr() is not intentionally contained, Cr() content rate is defined by chemical analysis in case T-Cr analysis is difficult with respect to plated parts including the entire surface layers such as chromate layer, or in case T-Cr amount is more than 1000ppm.</p> <p>Especially, there are cases when [hot liquid-proof / alkali-proof/ acid-proof] (organic or inorganic) extremely-thin coated layer is present. In such a case, sample extraction is difficult. Here, methods of analysis/ management which can address to such a case are described.</p>	
6-2-1-1. Initial detailed analysis: Analysis by diphenylcarbazide (after grind and collection)	
Preparation	Securing of samples <ul style="list-style-type: none"> • Prepare multiple samples when there is not enough area for analysis such as screw or spring, etc.
	Obtain data for content calculation <ul style="list-style-type: none"> • Obtain surface area and average thickness of a layer of target range for analysis (see Section 3)
	Determine sample collection domain <ul style="list-style-type: none"> • Basically, collect Cr() from tops of screws, where it can be easily collected, but do not collect Cr() from concave part where screw driver is applied. (Calculation is also easy)

	<p>Grind and collect method</p> <ul style="list-style-type: none"> • Articles needed for sample collection in particular are as follows: <ul style="list-style-type: none"> a. Cotton swab/ cotton swab (thin)/ tapered plastic stick (such as tip of a handle of F shaped dental floss wand, etc.) (F shaped dental floss wand with a fixed floss) b. Alkaline extraction buffer solution for EPA3060A c. Abrading agent (brown alumina which does not contain Cr #500) d. Membrane filter (approx. 0.2 ~ 0.45 μ m) • Dip a cotton swab, etc. into buffer solution, then attach a little amount of abrading agent to the cotton swab, and rub against the target point of the sample and grind it with the abrading agent until the color of chromate layer is discolored (In so doing, abrading agent and buffer solution will be scattered, all of which should be collected on a wide-mouthed container, such as a petri dish) • Sample from area which cannot be reached by a cotton swab such as the foot of a flange of a screw must be collected by grinding with a tip of tapered plastic stick in the same way. When sample from a cut part of a screw must be collected due to insufficient sample amount, grind and collect sample by grooves with dental floss in the same way (Abrading agent must be wet with buffer solution when grinding because the main reason for using buffer solution is to contain valence change of Cr when sample is ground) • After collecting sample, pour more than 20ml of buffer solution into a beaker, wipe the tip of tapered plastic stick several times with the aforementioned cotton swab used in the above, and rinse the tip of the stick in the solution in the beaker and take it out. When a dental floss is used, dip the part of the fiber which had contact with the target range of analysis into the beaker. • Put the cotton swab together with abrading agent and buffer solution collected in the petri dish into this beaker without leaving any leftover, and stir them for 30 minutes at 90 - 95 . • Take out the portion attached to the cotton swab and the fiber of a dental floss once at the end, and squeeze it out into the aforementioned beaker with hands wearing plastic gloves, and then dip it again in the liquid in the beaker, and squeeze it once again into the beaker.
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	<ul style="list-style-type: none"> • After keeping the beaker still , collect the supernatant fluid in this beaker, and prepare solution for analysis by filtrating with a membrane filter trying not to collect unnecessary metal which is not chromate layer (At this time, calculate the ratio of the weight of solution for analysis against weight of the buffer solution alone which was in the beaker in advance).
<p style="text-align: center;">Measurement</p>	<p>Analysis</p> <ul style="list-style-type: none"> • Adjust pH of aforementioned solution for analysis to appropriate value for coloring very carefully not to allow it to swing to too much acidity, and then quantify Cr() volume with diphenylcarbazide (Cr() detection weight of the solution for analysis) • Since normally a chromate layer is less than 1 μ m, calculate content rate of Cr() which exists in the target range for analysis, “plated layer + chromate layer” (See the following for the formula) $[\text{Cr() extracted weight}] = [\text{aforementioned Cr() detected weight}] / [\text{aforementioned ratio of the weight of solution for analysis}]$ <p>[Cr() content rate] = [Cr() extracted weight] / ([area for grinding and collection] X [weight per unit area of target range of analysis]</p> <p style="text-align: center;">(Note: At this time, weight of the chromate layer may be ignored)</p> <p>Analytical standard for reference: EPA3060A (Thermal alkaline extraction) IEC62321 (Thermal alkaline extraction [for plastic and electronic parts])</p>
<p>6-2-1-2. Management (analysis)</p>	
<p>Although it is desirable to implement aforementioned initial analytical form in periodical management, when it is confirmed that the surface does not repel acidum hydrochloricum of 4% concentration (Normally, the condition in which corrosion stain remains in all parts which had contact with acidum hydrochloricum after application of acidum hydrochloricum of 4% concentration), test if Cr() is present or not by using ion test paper, “Chrome Check A”, manufactured by Toyo Roshi Kaisha, Ltd. (ADVANTEC) (Note: “Chrome Check” in the same product series is not approved)</p> <ul style="list-style-type: none"> • Dip the aforementioned ion test paper into 4% acidum hydrochloricum in a blink, and immediately shake off unnecessary acidum hydrochloricum. • Stroke the chromate layer relatively widely with the aforementioned test paper which absorbed acidum hydrochloricum. • Wait for 30 seconds to confirm change of color to purplish red color. <p>If there is no color reaction in the aforementioned procedures, it is judged that there is no problem in qualitative level. (At this time, do not dissolve the plated layer in the substrate because color reaction may be obstructed by some element contained in the base material)</p>	

【For inquiry contact】

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