The RRF calculation results are shown in Table 2.

Table 2 Results of RRF calculation

Standard solution (ng/mL)	RRF
1020	0.907
255	0.876
51	0.905
5.1	0.939
0.51	0.872
Average RRF	0.89980
Standard deviation	0.02718
CV (%)	3.0

As shown in Figure 2, the favorable linearity was obtained within a range from 0.5 ng/mL to 1000 ng/mL. With the RRF variation coefficient at 3%, it is deemed that the calibration curve has been created with high accuracy.

The quantitation limit was estimated with the use of the standard solution for preparing the calibration curve with the lowest HCB concentration substantially lower than one-tenth the BAT level. The quantitation limit was obtained as a value 10 times the standard deviation from the HCB peak area obtained from the measurement results of the sample solution for the calibration curve (0.5 ng/mL: n = 5) with the lowest concentration. As a result, the conversion into the sample concentration (the quantity of the sample at 0.01 g for the constant volume of 50 mL) produced the quantitation limit of 0.08 μg/g, roughly one-125th of the BAT level (10 ppm), making the assessment of the concentration sufficiently possible. Figure 3 shows the SIM chromatogram of the standard solution for the calibration curve with the lowest condensation (0.5 ng/mL).

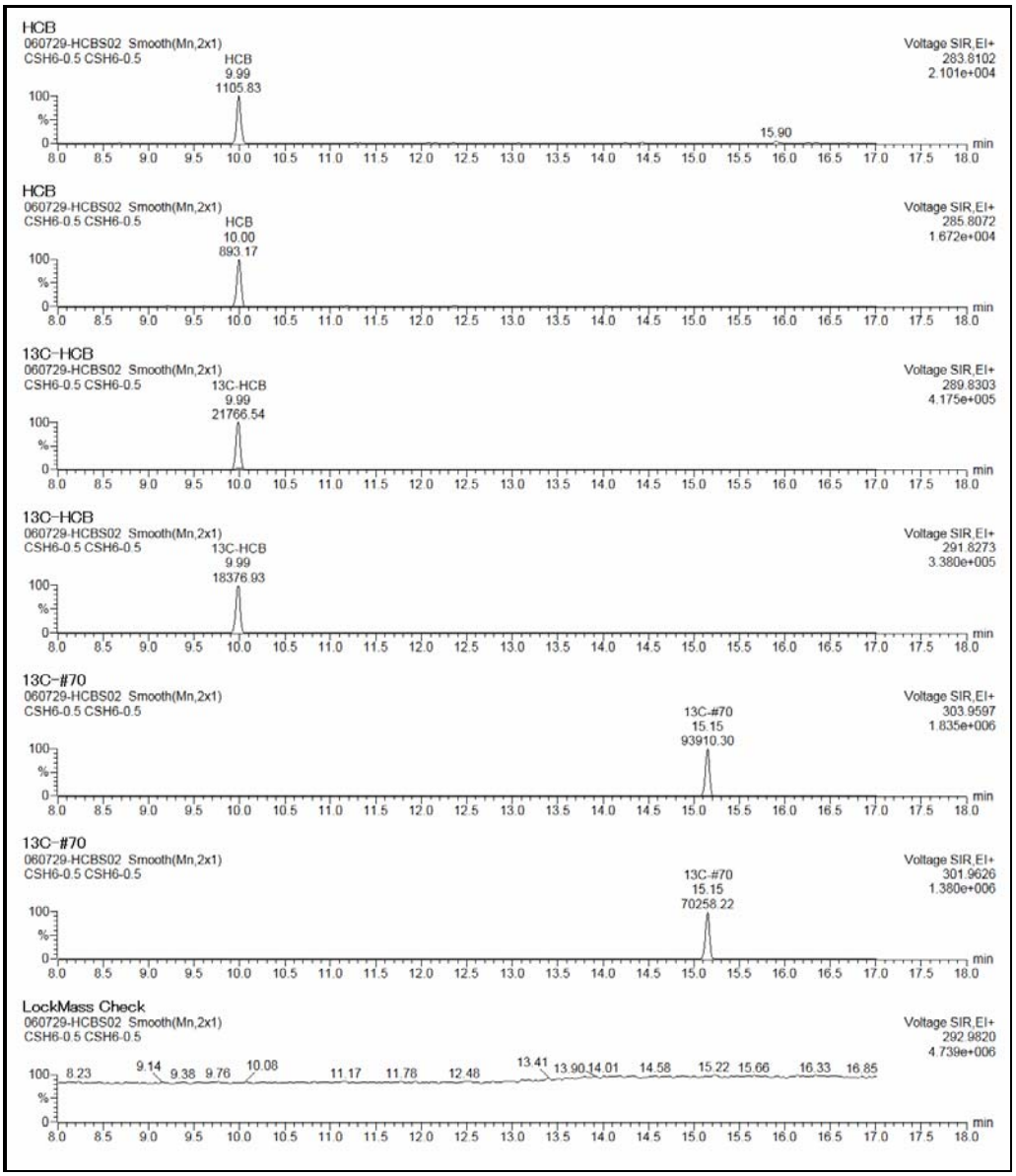


Figure 3　SIM chromatogram of the standard solution for the calibration curve with the lowest concentration

3. Method for quantitative determination

The quantity of the identified HCB (*Qi*) in the total volume of the extracted solution was obtained under the following formula (2) by using the internal standard method based on the added amount of the corresponding internal substance for cleanup spike.

$$\boxed{Qi = \frac{Ai}{Acsi} \times \frac{Qcsi}{RRF}} \quad \text{..... (2)}$$

Where, Qi: amount of HCB in the total volume extracted solution (pg)

Ai: peak area of HCB on the chromatogram

Acsi: peak area of the corresponding internal standard substance for cleanup spike

Qcsi: added amount of corresponding internal substance for cleanup spike (pg)

RRF: The relative response factor against the corresponding internal standard substance for cleanup spike

The HCB concentration of the sample was obtained under the following formula (3) on the basis of the quantity of HCB obtained.

$$\boxed{Ci = (Qi - Qt) \times \frac{1}{W} \times 10^{-6}} \text{..... (3)}$$

Where, Ci: The concentration of HCB in the sample (ppm)

Qi: amount of HCB in the total volume extracted solution (pg)

Qt: amount of HCB in blank test (pg)

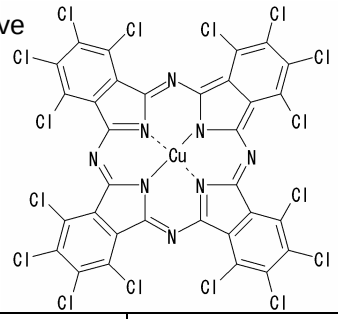
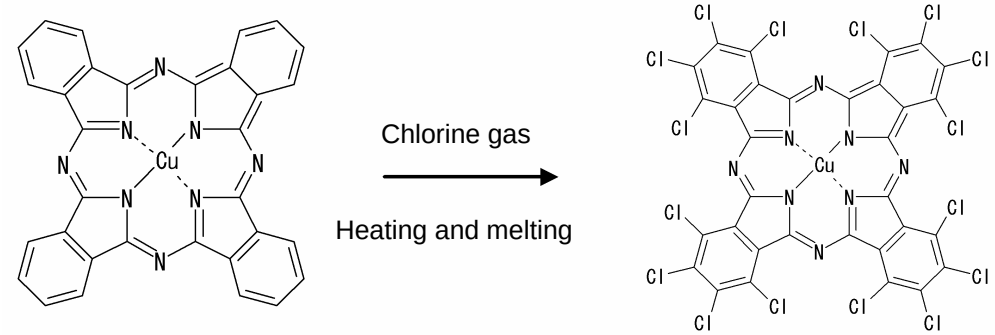
W: The quantity of the sample (g)

VI. Conclusion

1) It was found that an analysis with high response is possible under the method that dissolves a sample in sulfuric acid and corrects the HCB recovery rate with the use of internal substance.
2) The quantitation limit of this analytical method was 0.08 ppm

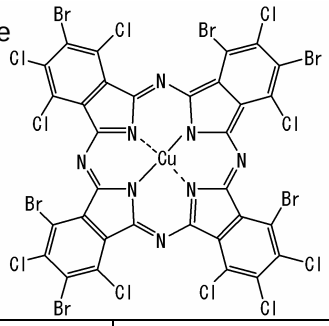
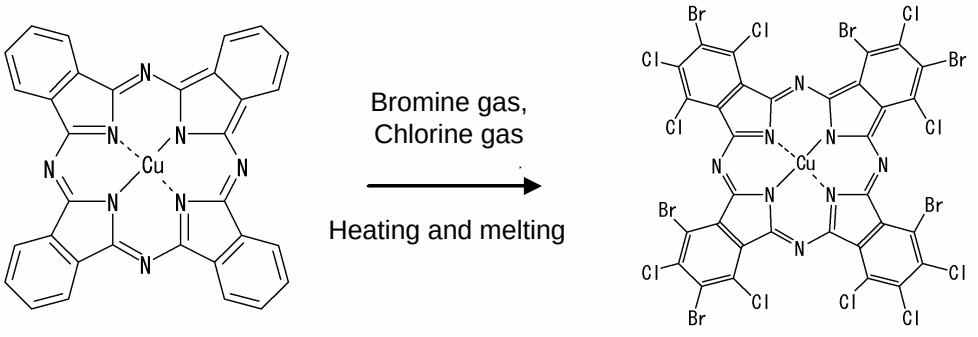
[Annex 9]

Description of Pigment Green 7

1	Structural formula			
	(Representative example) 	English name: C.I. Pigment Green 7 CAS registration number: 1328-53-6 , 14832-14-5 EINECS number: 215-524-7		
2	Composition formula	$C_{32}Cl_{16}CuN_8$ (Representative example)		
3	Molecular weight	1127.19 (Representative example)		
4	Low concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture			
	Category	Existing chemicals		
	CSCL No.	5-3315		
	Existing list Official Gazette publication name	Pigment Green 7		
5	Physicochemical property			
	Appearance	Green powder (provided by manufacturer MSDS)		
	Density	2.10 ± 0.20 g/cm^3 (provided by manufacturer MSDS)		
	Melting point	>350°C (CHRIP)		
	Boiling point	–		
	Vapor pressure	–		
	Water solubility	<0.1 g/L (20°C) (CHRIP)		
	LogPow	–		
6	Solubility in organic solvents (provided by manufacturer MSDS)			
	Methanol, butanol, MEK, xylene	Insoluble		
7	Manufacturing methods			
	The product is obtained by chlorinating molten Blue Crude with chlorine gas, precipitating in a precipitation tank, filtering, and cleansing with water.  Pigment Blue 15 Chlorine gas Heating and melting Pigment Green 7			

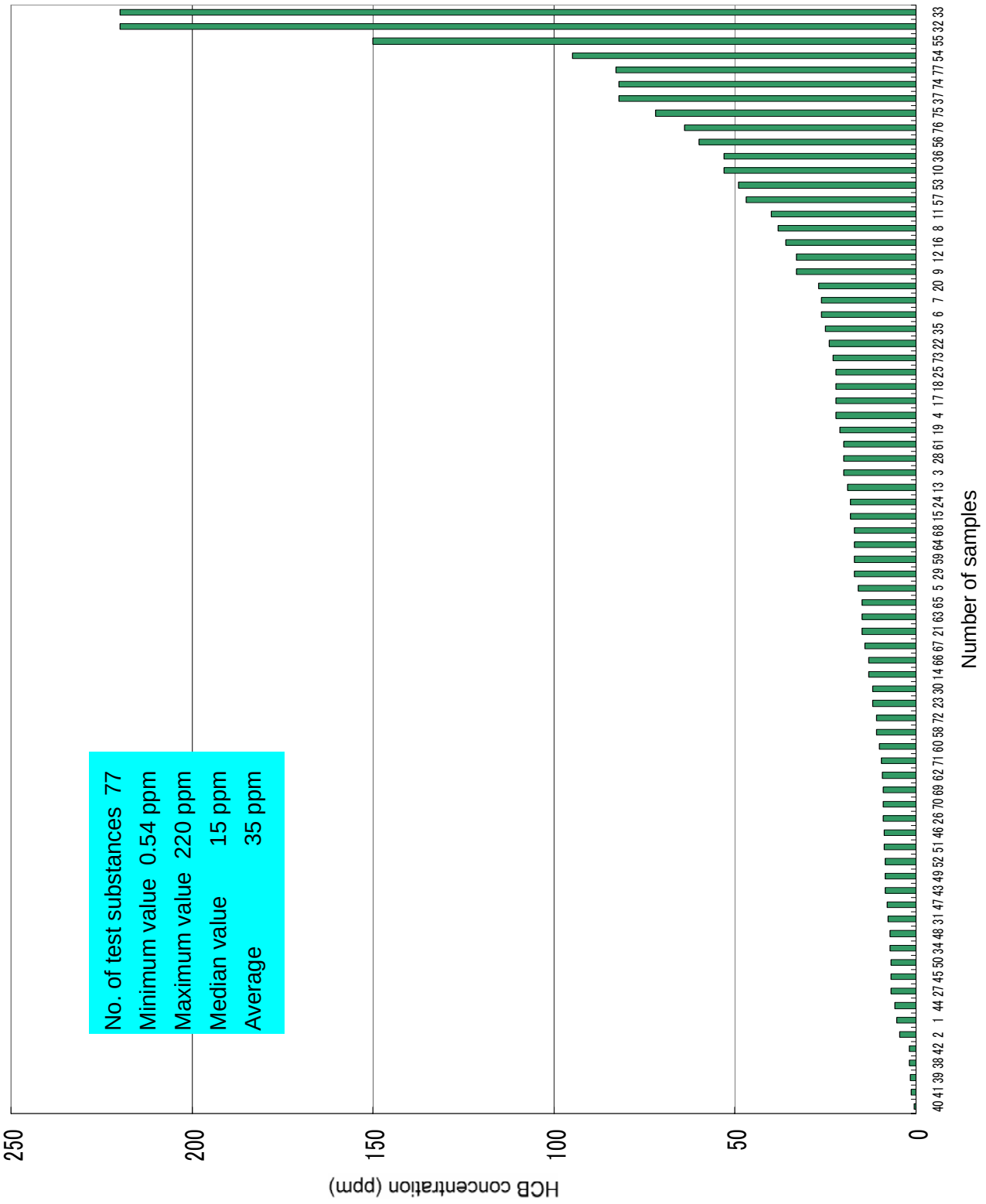
[Annex 10]

Description of Pigment Green 36

1	Structural formula			
	(Representative example) 		English name: Pigment Green 36 CAS registration number: 14302-13-7, 68512-13-0 EINECS number: 238-238-4	
2	Composition formula	$C_{32}Br_6Cl_{10}CuN_8$ (Representative example)		
3	Molecular weight	1393.9 (Representative example)		
4	Low concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture			
	Category	Existing chemicals		
	CSCL No.	5-3318		
	Existing list Official Gazette publication name	Pigment Green 36		
5	Physicochemical property (provided by manufacturer's MSDS)			
	Appearance	Green powder		
	Density	2.70 ± 0.30 g/cm^3		
	Melting point	–		
	Boiling point	–		
	Vapor pressure	–		
	Water solubility	Insoluble		
	LogPow	–		
6	Solubility in organic solvents (provided by manufacturer MSDS)			
	Methanol, butanol, MEK, xylene	Insoluble		
	Toluene	Insoluble		
7	Manufacturing methods			
	The product is obtained by brominating and chlorinating molten Blue Crude with bromine gas and chlorine gas, precipitating in a precipitation tank, filtering, and cleansing with water.  Pigment Blue 15 Bromine gas, Chlorine gas Heating and melting Pigment Green 36			

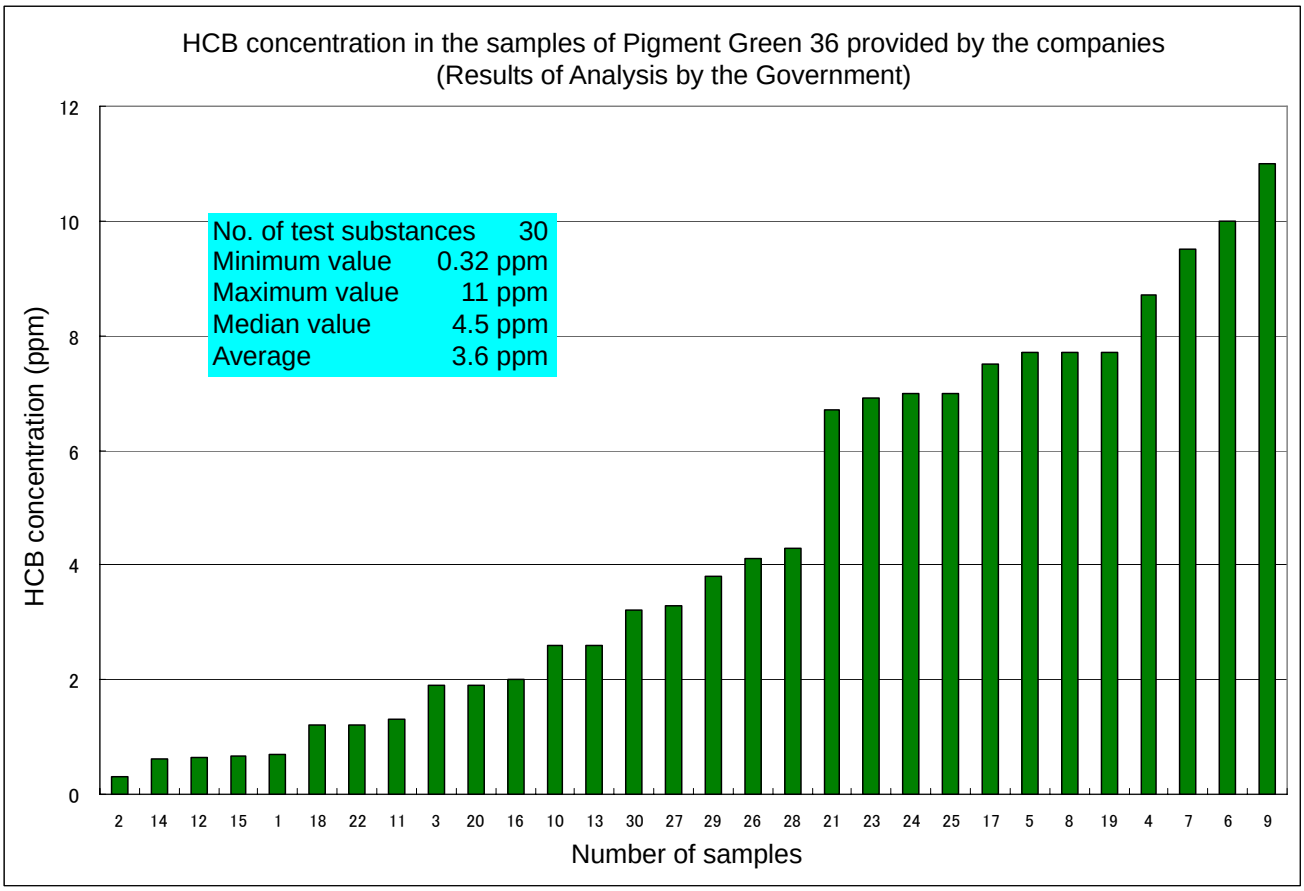
[Annex 11]

HCB concentration in the samples of Pigment Green 7
provided by the companies
(results of analysis by the government)



[Annex 12]

HCB concentration in the samples of Pigment Green 36
provided by the companies
(results of analysis by the government)



[Annex 13]

Examples of measurement of HCB content in phthalocyanine using GC/MS

I. GC/MS measurement conditions

Gas chromatograph (GC):	HP6890 (Agilent Technologies)
Mass spectrometer (MS):	AutoSpec-Ultima (Micromass)
Column:	ENV-5MS (internal diameter 0.25 mm, length 30 m, film thickness 0.25 μm, ; Kanto Chemical Co., Ltd.)
Oven temperature:	80 degrees Celsius (1 min.) → 20 degrees Celsius/min → 160 degrees C → 5degrees Celsius/min → 200 degrees C → 40 degrees Celsius/min → 280 degrees Celsius
Injection port temperature:	280 degrees Celsius
Carrier gas:	helium (steady flow volume mode at 1.5 mL/min)
Infusion quantity:	1 μL (splitless)
Transfer line temperature:	280 degrees Celsius
Ionization method:	Electron impact ionization method
Ion detection method:	Selected ion detection (SIM) method by Lockmass mode
Electron acceleration voltage:	36 V
Ionizing current:	500 μA
Ion source temperature:	280 degrees Celsius
Ion accelerating voltage:	8 kV
Resolution (10% valley):	10000
Accelerated voltage switching cycle:	0.59 second
Measured mass number:	set mass numbers are given in Table 1.

Table 1 Setting Mass Number

Target substances	m/z
HCB	283.8102 , 285.8072
$^{13}C_6$-HCB	289.8303 , 291.8273
$^{13}C_{12}$-TeCB	301.9626 , 303.9597

II. Preparation method for sample solution

0.01 g of a sample was dissolved in sulfuric acid for a constant volume of 50 mL. Then, 1 mL was taken out to which 4 mL of hexane and a known quantity of cleanup spike ($^{13}C_6$-HCB) were added, followed by the liquid extraction for taking out the hexane layer. After repeating the procedure twice, the hexane layer obtained was concentrated to some 1 mL for the cleanup using silica gel cartridges (Spelclean made

by Supelco, LC-Si 6 mL glass Tube, 1 g). After concentrating 10 mL of the hexane eluate obtained, the syringe spike internal substance ($^{13}C_{12}$-TeCB (#70), nonan solution) was added to make it 50 μL for use as sample solution.

III. Preparation of the calibration curve

The concentration of HCB standard solutions prepared with nonane was ranged from 0.5 ng/mL to 1000 ng/mL gradually. The concentration of the internal substance in the standard solution for preparing the calibration curve was all set at 10 ng/mL for $^{13}C_6$-HCB and 25 ng/mL for $^{13}C_{12}$-TeCB.

IV. Quantitative determination and confirmation

1 μL of sample solution was taken out to be infected in the GC/MS to form the SIM chromatogram. If the retention time of the HCB peak on the chromatogram was the same and the peak area ratio of the two monitor ions was equivalent to the area ratio of the isotope, it then was identified as HCB and its quantity was determined.

V. Results and Discussion

1. Consideration of analytical conditions

Figure 1 shows SIM chromatograms of HCB analysis in the samples of phthalocyanine pigments (example of Pigment Green 36)

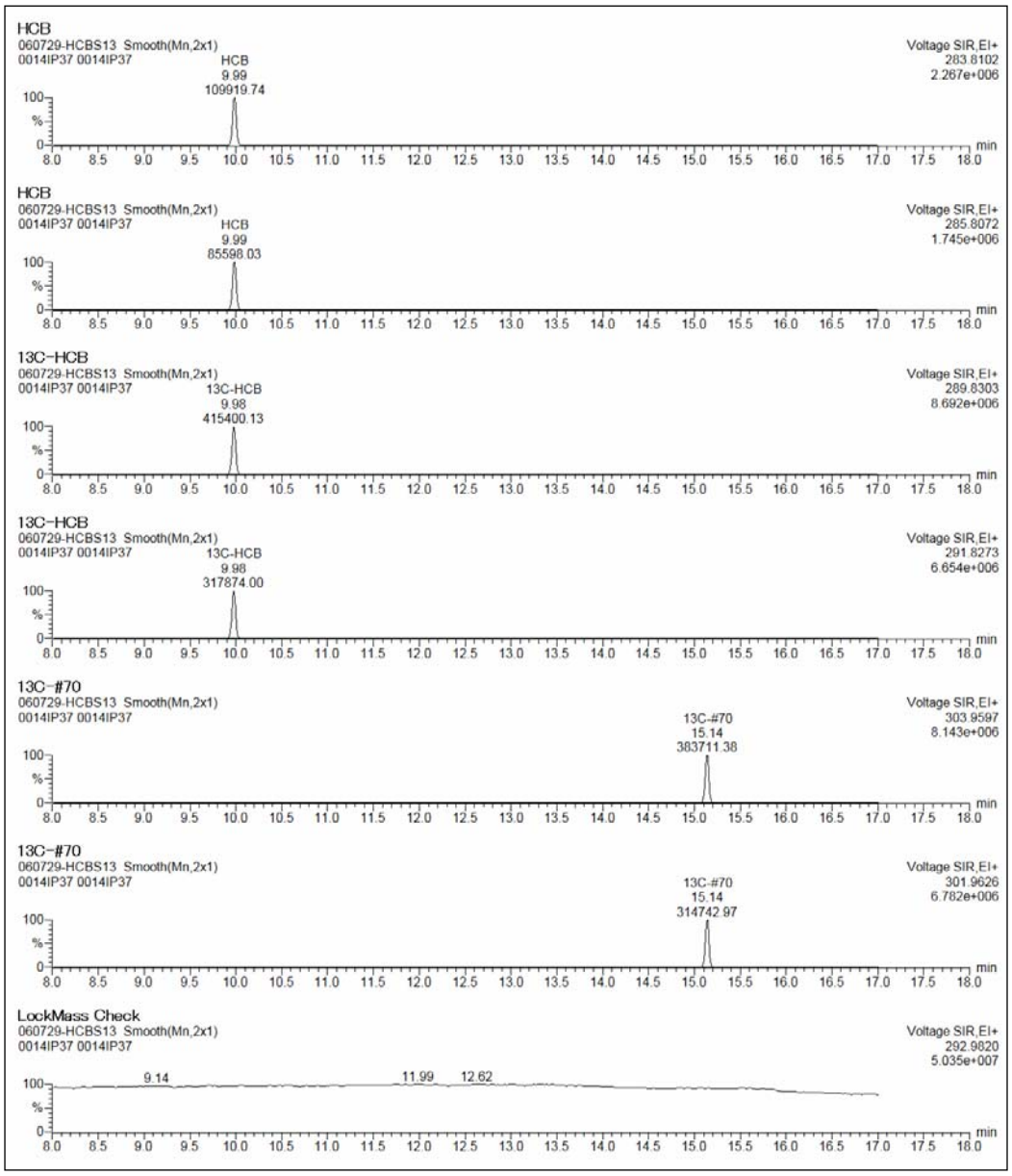


Figure1 SIM chromatograms of HCB analysis in the samples of Pigment Green 36

The lockmass variable chart at the bottom of Figure 1 is stable to indicate the favorable purification of the sample solution through the cleanup procedure.

2. Calibration Curve and Quantitation Limit

The peak area ratio of the standard substance to the reference substance in the cleanup spike was calculated by obtaining the peak areas of the standard substance and the internal substance for cleanup spike. Using this peak area ratio and the concentration ratio between the standard substance in the standard solution and the cleanup spike, the calibration curve was formed to calculate the relative response factor (RRF). The RRF value was calculated for all concentrations on the calibration curve with the following formula (1).

$$\boxed{\mathrm{RRF} = \frac{\mathrm{Qcs}}{\mathrm{Qs}} \times \frac{\mathrm{As}}{\mathrm{Acs}}} \quad \text{..... (1)}$$

Where, RRF: Relative response factor of the measuring target substance against the internal substance for cleanup spike

Qcs: amount of the internal substance for cleanup spike in the standard solution (ng)

Qs: amount of the measuring target substance in the standard solution (ng)

As: peak area of the measuring target substance in the standard solution

Acs: peak area of the internal substance for cleanup spike in the standard solution

Figure 2 shows a plot of the peak area ratio versus the concentration ratio

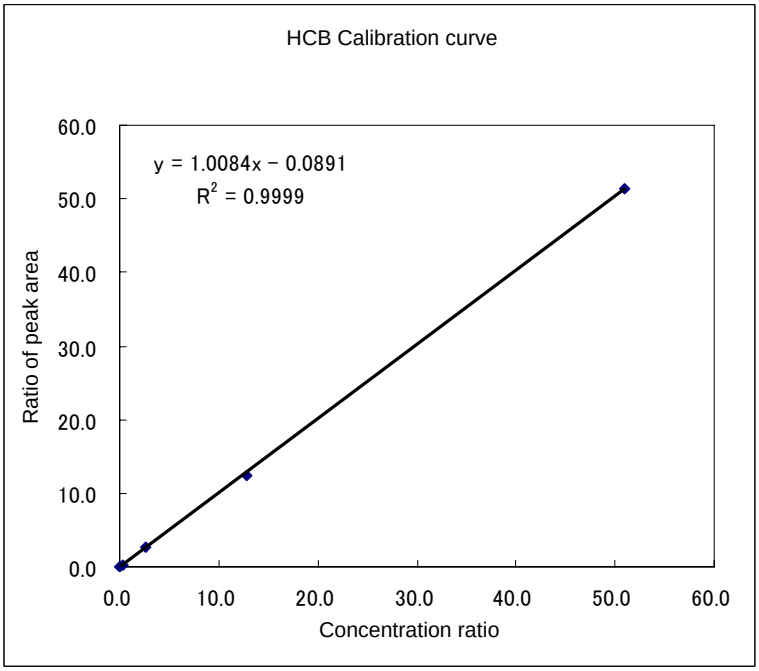


Figure 2 HCB calibration curve

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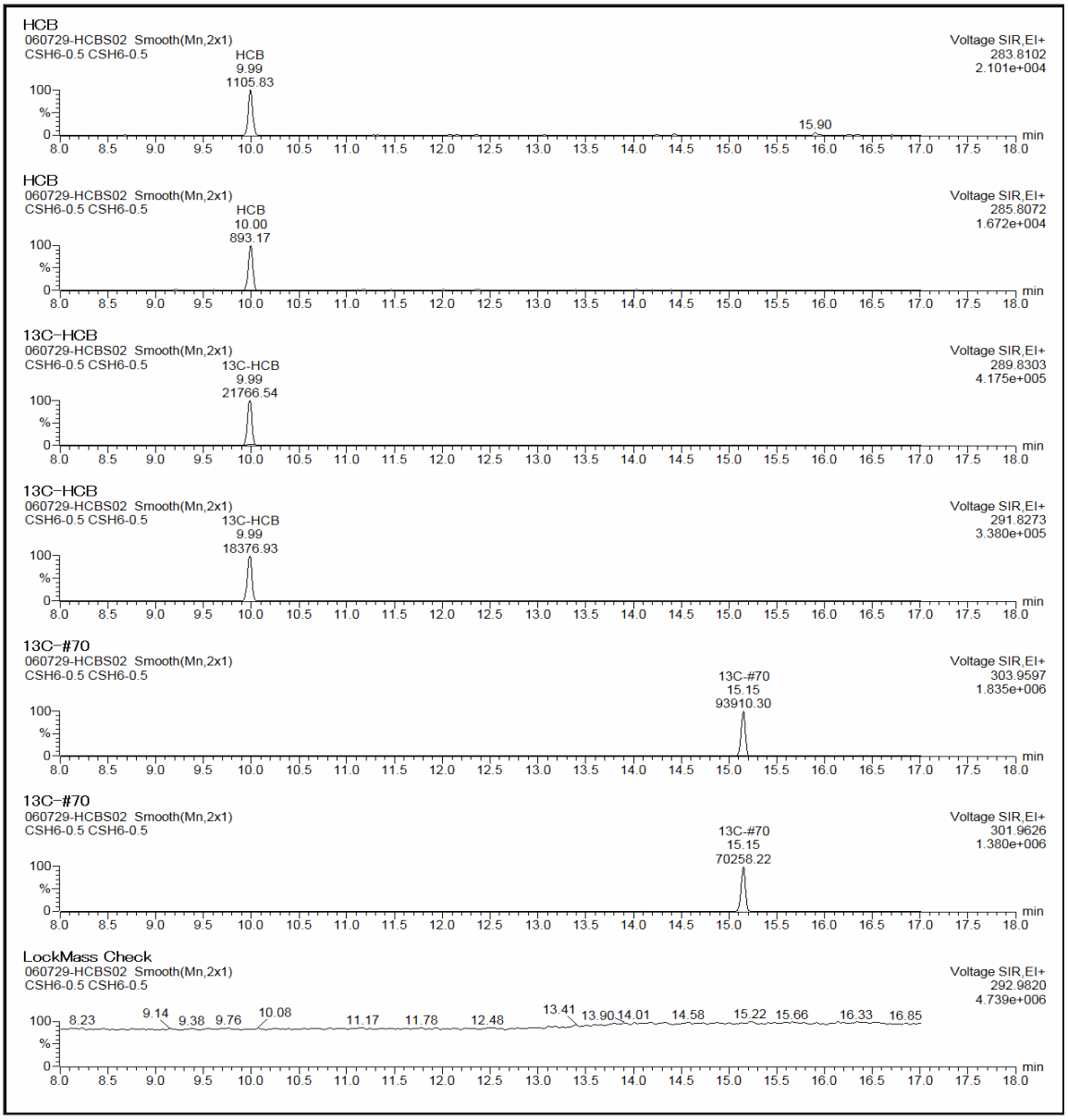

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$$\boxed{Ci = (Qi - Qt) \times \frac{1}{W} \times 10^{-6}} \text{..... (3)}$$

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VI. Conclusion

1) It was found that an analysis with high response is possible under the method that dissolves a sample in sulfuric acid and corrects the HCB recovery rate with the use of internal substance.
2) The quantitation limit of this analytical method was 0.08 ppm