Report on BAT Levels concerning By-product HCB in Other Pigments Derived from TCPA and Phthalocyanine Pigments

(Provisional translation by the government)

April 2007

Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product

[Table of Contents]

Part I Background of the Study

Part II The BAT levels for other pigments derived from TCPA

Part III The BAT level for phthalocyanine pigments

(Note: The Committee collected information necessary for preparing this report through hearings with the companies concerned. However, as some of the information involves trade secrets, this report does not include specific information pertaining to such secrets.)

Part I Background of the Study

1. Introduction

This report summarizes the results of the study obtained after November 2006 by the Assessment Committee on BAT levels for Reduction of a Specified Chemical as a Contaminant By-product (hereinafter referred to as the Committee) established by the Ministry of Health, Labour and Welfare (MHLW), the Ministry of Economy, Trade and Industry (METI) and the Ministry of the Environment (MOE) (hereinafter referred to as the Three Ministries).

For the details of the issue of by-product hexachlorobenzene (hereinafter referred to as HCB) and establishment of a committee, refer to Part I of Report on BAT Levels for By-product HCB in TCPA and Solvent Red 135 (hereinafter referred to as the First Report). Annex 1 describes the details of the Committee meetings for the preparation of this report and the committee members.

2. Background of the study concerning other pigments derived from TCPA

The First Report proposed by-product HCB levels that are technically and economically attainable in chemical substances (hereinafter referred to as BAT Levels) as follows: 200ppm for tetrachlorophthalic anhydride (hereinafter referred to as TCPA); 10ppm for Solvent Red 135 among the dyes and pigments produced using TPCA as the raw material (hereinafter referred to as SR 135). Based on the report, the Three Ministries presented the view that it is appropriate to regard the value 10ppm, which is the BAT Level for SR 135, as the BAT Level for dyes and pigments other than SR 135 for the time being and decided to continue to study whether it is appropriate to use the value “10ppm” as the BAT Level for other pigments derived from TCPA that currently contains more than 10ppm of HCB.

In accordance with this policy, after publishing the First Report, the Committee studied the BAT Levels for other pigments derived from TCPA, which had been proved to contain more than 10ppm of HCB, by conducting hearings with manufacturers and importers of such pigments. Part II of this report summarizes the results of study.

3. Background of the study concerning phthalocyanine pigments

In March 2006, it was made clear that the dyes or pigments made by chlorinating Pigment Blue 15 (Official Gazette Notice No.5-3299、CAS No.149-14-8)(hereinafter referred to as “phthalocyanine pigments”) also contained by-product HCB.

As of April 6, 2006, the Three Ministries adopted a policy that the Committee should study whether it is necessary to set a BAT Level for HCB in phthalocyanine pigments for manufacturers and importers of phthalocyanine pigments and that the BAT Level should be established as early as possible if that were deemed necessary. The Three Ministries also requested relevant companies to take the best possible measures to reduce the HCB content and to strictly control and report the production, import, sales, and storage of such products.

After publishing the First Report, the Committee carried out a study on the above-mentioned Section 2, and, at the same time, studied the BAT Level for phthalocyanine pigments by conducting hearings with manufacturers and importers of phthalocyanine pigments. The results of the study are summarized in Part III of this report.

4. Basic approach to specified chemical substances as by-products

The basic approach to specified chemical substances as by-product (approach based on the concept of BAT) is as described in Part I, Section 2 and other parts of the First Report. Since the approach is also the basis of this report, the description is reproduced below.

> Class I specified chemical substances regulated under CSCL do not decompose easily by natural processes in the environment (being persistent), tend to accumulate in biotic bodies (being highly accumulative), and have long-term toxicity against humans and/or higher predatory animals. Since it is hard to monitor and prevent the progress of environmental pollution by Class I specified chemical substances once they are released into the environment, they may potentially cause health hazards.
>
> Consequently, from the standpoint that the generation of Class I specified chemical substances produced as by-products in the manufacture of chemical substances should be constrained as much as possible, CSCL assumes the stance that the “Best Available Technology/Techniques” (BAT) should be applied to reduce Class I specified chemical substances to a “technically and economically feasible level” (hereinafter referred to as the “BAT level”) (see Annex 2 and Annex 3 for details about BAT).
>
> This is because it is assumed that taking particular care to curb the release of Class I specified chemical substances into the open system is the minimum obligation imposed on chemical manufacturers and those who allow their products to contain the specific chemical substances, even as an impurity, beyond the technically and economically feasible levels, are deemed to be manufacturing Class I specified chemical substances through negligence of such a duty.

Normally, in the industrial production of chemicals, there are incentives to produce higher quality (containing fewer impure substances) products amid free competition. Even when Class I specified chemical substances are generated as by-products, the content of Class I specified chemical substances is assumed to converge with a technically and economically feasible level of reduction through such efforts to enhance the value of products and efforts in line with the above-mentioned duty.

Given the characteristics of Class I specified chemical substances mentioned earlier, when the generation of a Class I specified chemical substance as a by-product is technically unavoidable in the manufacture of a certain chemical substance, and if there exists a safer substitute substance that has the same function as the said chemical substance, and that does not generate any Class I specified chemical substance in the process of production, then it goes without saying that it is desirable to curb the generation of Class I specified chemical substances to zero through substitution.

Part II The BAT Levels for other pigments derived from TCPA

1. Description of other pigments derived from TCPA

Other pigments derived from TCPA that were studied (by conducting hearings) and proved to contain HCB in a concentration of more than 10ppm were the following three compounds.

(1) Pigment Yellow 110 (CSCL No. 5-3185,CAS No.5590-18-1)
(2) Pigment Yellow 138 (CSCL No. 5-5281,CAS No.30125-47-4)
(3) Pigment Red 257 (CSCL No. 5-5746,CAS No.117989-29-4,70833-37-3)

However, since the companies reported that they would stop selling (3) because they were endeavoring to replace it with an alternative, the Committee did not study the BAT Level for (3).

The structural formula and physicochemical properties of Pigment Yellow 110 (hereinafter referred to as PY 110) and Pigment Yellow 138 (hereinafter referred to as PY 138) are as described in Annex 4 and Annex 5 respectively. Domestic shipments of PY 110 and PY 138 in 2005 were several hundred tons and some 100 tons respectively.

PY 110 and PY 138 are used, separately or mixed with other pigments, for coloring of plastic products, coating materials and inks. Major applications of the plastic products colored with PY 110 and PY 138 include construction materials and convenience goods; and coating materials are used for exterior painting of automobiles. Judging from the use of them and the concentrations of impurity HCB in final products, the use of final products is unlikely to have any direct impact on human health. In view of the final uses, however, the companies concerned confirmed this as an extra precaution.

Generally speaking, it is difficult to replace dyes and pigments with alternatives immediately because of the changes in the hue and durability. This is also true for PY 110 and PY 138 and replacement is difficult because no alternatives comparable to PY 110 and PY 138 in terms of weatherability have been developed.

2. Basic approach to the study of BAT levels

According to the First Report, HCB is generated in the TCPA manufacturing process, and the HCB contained in SR 135 derives from the HCB generated in the synthetic process of the raw material TCPA as a by-product; therefore, to reduce the content of HCB in SR 135, the most effective and efficient measures are to reduce the HCB contained in TCPA. On the assumption that the BAT Level for TCPA is 200ppm, the value “10ppm” has been introduced as the BAT Level for SR 135.

Based on the results of the study described in the First Report, the BAT Levels for other pigments derived from TCPA in this report are studied:

(1) First, it is checked whether HCB is generated as a by-product in the manufacturing process for each pigment.
(2) Then, based on the BAT Level of TCPA, the concentrations of HCB (in other words, how much the concentrations of HCB in other pigments derived from TCPA would be when TCPA containing HCB at a concentration of 200ppm or less is used as the raw material) is studied on the basis of information collected from companies.
(3) If there are effective measures other than reducing the HCB content in raw material TCPA, such measures are taken into consideration.

3. HCB contamination level

As for the concentration of HCB in PY 110 and PY 138, in addition to the analysis results provided by manufacturers, importers, and users, the government conducted analysis of samples collected from companies that had stocks of these compounds (see Annex 6 and Annex 7). According to the result, 34-190ppm of HCB (one-millionth (mg/kg) on a weight basis; the same is applied hereinafter in this report) was found in PY 110 samples and 52-94ppm of HCB was found in PY 138.

In some cases, the analytical results provided by the companies differed from those obtained by the government. The following factors are thought to be the causes of the difference.

(1) Difference in the extraction process for HCB from the pigment

    Although most of the manufacturing companies and analytical laboratories extract HCB by liquid-liquid extraction with hexane after the pigment is dissolved in concentrated sulfuric acid, some analytical laboratories extract HCB by directly adding an organic solvent in the pigment and using ultrasonication. When ultrasonic extraction using an organic solvent is applied, the analytical values tend to be lower compared with those obtained by sulfuric acid dissolution because the HCB inside the pigment cannot be completely extracted.

(2) Outside the range of calibration curve

    Some results were higher than the results obtained by the government because the analysis was made outside the concentration range of the calibration curve.

Considering the above-mentioned causes for analysis errors, it seems appropriate to present a specific standardized analysis method for confirming the concentration level when establishing the BAT Level (see Section 10 described later).

4. Generation of by-product HCB in the manufacturing process for other pigments derived from TCPA

The results of a study based on the reports from the companies shows that the generation of by-product HCB in the production process of PY110 and PY138 is not confirmed as in the case of SR135; therefore, it is thought that the part of HCB contained in the raw material TCPA remains unchanged in the pigments

5. HCB concentration based on the assumption of the BAT level for TCPA

(1) PY110

According to the information obtained from the companies concerned, test results indicate that the HCB concentration in PY110 can be reduced to 10ppm or less when TCPA containing HCB of BAT Level (200ppm) is used as the raw material. However, to use TCPA containing HCB of 200ppm or less, since it is necessary to modify the production line due to the change in the raw material, the companies intend to put the process to practical use by the end of 2007.

(2) PY138

According to the information from the companies concerned, HCB concentration in the TCPA presently used as the raw material is in the range of 1000-2000ppm, which is relatively high, and it is necessary for them to stock TCPA for at least one year in order to continue stable supply to customers of PY138 in various countries and regions. Although it is expected that the use of TCPA containing HCB at a concentration lower than the BAT Level would prove to be effective for the reduction of HCB in PY 138, the actual possible reduction of HCB when TCPA containing less HCB is used as the raw materials, it will be made clear in about six months after the tests confirming the effects of the use of TCPA containing HCB at a lower concentration than BAT Level on the production process and quality of PY138. It was also reported that the most important point is to secure a stable supply of raw materials of consistent quality.

6. HCB reduction measures in the manufacturing process for other pigments derived from TCPA

(1) PY110

The companies concerned have reported that HCB concentration is reduced by increasing the number of washings in the manufacturing process for PY 110. However, since an only increase in the number of washings cannot significantly reduce the HCB concentration, it is indispensable to use TCPA that contains a low level HCB, and the combination of the use of low-HCB concentration TCPA and the increase in the number of washings will efficiently and effectively reduce HCB.

(2) PY138

From the viewpoint of reducing the HCB concentration, there is a report that a reduction in HCB by some 10ppm was observed by washing PY138 with aromatic organic solvents and halogen solvents experimentally. However, from the viewpoints of occupational safety, fire prevention, and contamination of the environment, it is undesirable to introduce these solvents into the manufacturing process newly. For this reason, no reports are found that describe effective measures for reducing HCB in PY 138 other than the use of TCPA with a low HCB concentration.

7. The BAT level for HCB in other pigments derived from TCPA

To reduce the HCB concentration in PY 110 and PY 138, the most important and effective measure, as in the case of SR 135, is to reduce the HCB content in the raw material TCPA. The results of hearings confirmed that it is technically possible to reduce the HCB concentration in PY 110 down to 10ppm by using TCPA with an HCB concentration of 200ppm, which is the BAT level of TPCA, or lower as the raw material. Furthermore, As in Section 5.(1) stated above, reduction to 10ppm seems to be economically feasible since the companies concerned have established a target to reduce the HCB concentration in the PY 110 they supply down to 10ppm by the end of 2007, and they have a favorable outlook for the achievement.

On the other hand, with regard to PY 138, the HCB concentration which is achievable when using TCPA that meets the BAT Level has not been made clear at present. However, it has been confirmed that the use of TCPA with a low HCB concentration is an effective way of reducing HCB in PY 138. The companies concerned intend to continue tests on a production scale using TCPA with an HCB concentration less than the BAT Level to confirm the stable procurement of such TCPA and the stability of the quality of PY 138 so that the technology is put to practical use. Although details have not been clarified and studies by the companies must be continued to come to a final conclusion, at present, since the HCB concentration in the TCPA used as the raw material for PY 138 is 1000-2000ppm, which is relatively high, it is expected that the reduction in HCB concentration in PY 138 can be fully achieved by replacing the present TCPA with that containing HCB of BAT Level.

Therefore, it is appropriate to set the BAT Level for PY 110 to 10ppm as in the case of SR 135 and other pigments and dyes derived from TCPA. As for PY 138, on the other hand, although sufficient information to reach a final conclusion has not been collected, the basic measures for reducing HCB are the same as those for other pigments derived from TCPA. It is therefore desirable to set the BAT Level to 10ppm. In order to assess whether the value of 10ppm is achievable level, detailed studies must be continued based on the studies of the companies concerned. Until a final decision is made, it is appropriate that companies will continuously control to reduce by-product HCB by self-monitoring, and that the government will properly assist implementation by the companies concerned.

8. Positioning of BAT level and future treatment

As pointed out in the First Report, after the implementation of the proposed BAT Level, the manufacture, import, or use of the other pigment derived from TCPA containing HCB concentrations higher than such BAT Level would not be permitted under CSCL. The results of the study down to Section 7. described above, indicate that "10ppm," which is the BAT Level for Solvent Red 135 proposed by the First Report, can be applied to other pigments derived from TPCA except for PY 138.

Consequently, we once again propose, combining the conclusions of the First Report, that the BAT Level for all the pigments derived from TCPA except for PY 138 be set to "10ppm." Regarding PY 138, it is necessary for the companies concerned to study the possibility of using TCPA with an HCB concentration level 200ppm or less and report the results to the government as early as possible. At the same time, it is also necessary for the Three Ministries to grasp the current status of studies being conducted by the companies and assess whether 10ppm is a practical level as the BAT, and to take appropriate measures including another consultation with the Committee as required.

Since it is indispensable for the achievement of an HCB concentration level of 10ppm that TCPA with a concentration of 200ppm (BAT Level) or less is stably supplied, it is appropriate to set a certain get-acquainted period before the proposed BAT Level comes into force as in the case of SR 135.

Meanwhile, after the publication and entry into force of the proposed BAT Level, manufacturers of other pigments derived from TCPA are being called upon to exert consistent efforts to supply TCPA with as low as possible HCB concentration regardless of the proposed BAT Level.

It would be appropriate for the government to continue to strive to collect related information even after the implementation of the proposed BAT Level and convene the Committee periodically in order to reconsider and review the BAT Level on the basis of newly obtained information.

Furthermore, users of other pigments derived from TCPA (companies that dye plastics and other materials using such pigments, for example) should fully recognize that HCB is a Class I specified chemical substance, and are therefore strongly expected to strive to procure and use TCPA with a HCB concentration less than the proposed BAT Level.

9. Proper treatment of HCB removed in the manufacturing process for other pigments derived from TCPA

In the manufacturing process for the other pigments derived from TCPA (including other pigments derived from TCPA other than PY 110 and PY 138 that are the subjects of the present study), it is expected that most of the by-product HCB contained in the raw material TCPA is transferred to the reaction solvent (filtrate after the reaction). Therefore, it is essential for manufacturers of other pigments derived from TCPA to fully recognize this fact and appropriately manage and treat reaction solvents after the reaction is completed and, at the same time, adopt a strict treatment protocol to prevent workers engaged in the process from being exposed to HCB.

It is also possible that a small amount of HCB will be contained in the water discharged from the cleansing process after the reaction of the other pigments derived from TCPA, although the amount is smaller compared to that of the reaction solvent. Therefore, it is necessary to check the water discharge by means of periodic analysis and take appropriate measures, as reqired, for wastewater treatment to control discharge of HCB into the environment and to prevent environmental pollution.

10. Analytical technique for HCB contained in other pigments derived from TCPA

The First Report proposed an analytical method for the analysis of HCB in SR 135 based on the fact that SR 135 is insoluble in many organic solvents (see Part III, Section 10 and Annex 10 of the same report). Basically, it is also appropriate that this method can be applied to the analysis of other pigments derived from TCPA (excluding SR 135). Further, since the method will prevent the errors arising from the use of different analytical methods described in Section 3 above, it is represented below as the “Analytical technique for HCB contained in other pigments derived from TCPA.”

For the quantitative analysis of HCB contained in the pigments derived from TCPA, a method with a quantitation limit that provides stable measurement of concentrations less than one-tenth (1ppm) of the BAT Level (10ppm) must be adopted.

Since the pigments derived from TCPA are insoluble to most of the organic solvents, the pigments do not dissolve during Soxhlet extraction using toluene or ultrasonic extraction so that the HCB content tends to be estimated at a lower value because the HCB contained inside is not extracted.

Therefore, as described below, an appropriate method for analysis is to take a precise amount of a sample and extract HCB using an organic solvent such as hexane or toluene after dissolving the sample in a sulfuric acid solution of constant volume. Then the solution is analyzed using a gas chromatograph/electron capture detector (GC/ECD) or gas chromatograph/mass spectrometer (GC/MS)(see Annex 8).

In order to ensure the accuracy of analysis, confirm beforehand that the method is appropriate by performing recovery ratio measurements and blank tests. Since HCB is a Class I specified chemical substance, avoid inhalation, accidental ingestion, and direct contact with the skin, and ventilation of the pretreatment rooms and analysis rooms. The waste fluid, and waste must also be appropriately controlled. Since other chemicals and solvents may also cause damage to the operator's health due to inhalation or accidental ingestion, the samples must be handled carefully and sufficient ventilation of the laboratory should be provided. When taking samples, as much effort as possible should be exerted to ensure the representativeness of the samples.

(1) Sample preparation procedure

Take a precise amount of a sample of pigment derived from TCPA, dissolve it into a sulfuric acid solution, and mix it thoroughly. Transfer the sample solution to a volumetric flask and obtain a constant volume by filling the volumetric flask with the sulfuric acid solution up to the marked line. Confirm visually that the pigment derived from TCPA is completely dissolved. If necessary, take a suitable aliquot of the sample solution and add a known quantity of an internal standard substance in consideration of the detection range of the equipment used. Extract HCB in the sulfuric acid solution with a solvent such as hexane or toluene. Purify the extract liquid as necessary as a measurement sample. The purification methods include additional sulfuric acid treatment and water washing, use of silica gel cartridges, and/or a combination of these methods. It should be noted that the absence of purification could cause the deterioration of the GC injection port and analytical columns. Since HCB recovery rate may deteriorate in the extraction and purification process, it is necessary to consider beforehand appropriate sample preparation methods that can ensure a sufficient level of HCB recovery. When the sample solution is dried at the time of concentration by nitrogen gas flow or other methods, the HCB recovery rate declines substantially. Internal standard substances that can be analyzed under the same conditions as HCB should be adopted in the sample preparation. When GC/ECD is selected as the measurement equipment, it is necessary to adopt substances whose retention time is different from that of HCB. For this purpose, γ-HCH (lindane) or other substances can be used. In the GC/MS (SIM) analysis, $^{13}C_6$-HCB, which is labeled with ^{13}C, may be used as the internal standard substance. It is also necessary to confirm in advance that the reagents used for the analysis are appropriate for the analysis through blank tests.

(2) Measurement procedures

a) Setting up the measurement conditions

Set conditions for the instruments so that the HCB peak can be separated in a good condition from other chemical compounds on the chromatogram and that it responds in a stable manner. Especially, care should be taken since chemical compounds other than HCB exist in the sample for the measurement. It is necessary to confirm that HCB analysis is not affected by interference from other impurities by conducting GC/MS to detect all the ions. If interference exists, further purification of the sample and/or changes in analytical conditions (type of analytical columns used, temperature raising condition, etc.) are needed. When $^{13}C_6$-HCB is used as the internal standard substance, extra care must be taken in the setting of measuring mass number because ions derived from HCB interfere with low-resolution GC/MS analysis. While M+2 and M+4 ions are usually measured, a resolving power of over 10,000 is required to prevent the interference of HCB contained in the sample with the internal standard. When low-resolution GC/MS is used, it is necessary to measure M+6 and M+8 ions or use internal standard substances other than $^{13}C_6$-HCB.

b) Preparation of calibration curve

Inject a certain quantity of the standard HCB solution prepared in advance for calibration curves into the GC, and create a calibration curve from the relationship between the HCB peak area and concentration obtained. As for the concentration of the standard solution, it is required that the concentration of HCB in the sample calculated on the basis of the quantity of the sample of the pigment derived from TCPA and the quantity of the solvent dilution include the BAT Level and that linearity of the calibration curve using standard solutions with three or more concentration levels should be secured. When an internal standard substance is used, HCB concentration is determined by the response factor (RF) method or a calibration curve using the internal standard.

c) Quantitation limit

The quantitation limit is estimated using the standard solution for preparing calibration curves with the lowest HCB concentration that is lower than one-tenth the BAT Level. More specifically, the standard solution for preparing the calibration curve with the lowest HCB concentration is analyzed repeatedly, at least five times, then the standard deviation is calculated on the basis of the obtained measurement values and the quantitation limit is set at a level tenfold of this standard deviation. A quantity of a sample and its constant volume needs to be set so that the HCB concentration of the measurement sample calculated on the basis of the quantitation limit should be a value less than one-tenth the BAT Level.

d) Quantitative determination of HCB

The chromatogram is obtained by injecting the measurement sample into the GC. If the retention time of the peak on the chromatogram is almost the same as that for the standard substance, quantitative determination of HCB can be made.

Part III The BAT level for phthalocyanine pigments

1. Description of phthalocyanine pigments

The phthalocyanine pigments investigated (hearings) in the present study are the following three:

(1) Pigment Green 7 (CSCL No.5-3315, CAS No.1328-53-6, 14832-14-5)
(2) Pigment Green 36 (CSCL No.5-3318, CAS No.14302-13-7, 68512-13-0)
(3) Pigment Blue 76 (CSCL No.5-6613, CAS No.68987-63-3)

However, since the companies reported that (3) is not being produced now and they are considering halting the use of it, the Committee did not investigate the BAT Level of (3).

The structural formula and physicochemical properties of Pigment Green 7 (hereinafter referred to as PG 7) and Pigment Green 36 (hereinafter referred to as PG 36) are described in Annex 9 and Annex 10 respectively. Domestic shipments of PG 7 and PG 36 in 2005 amounted to some 1,200 tons and some 300 tons respectively.

PG 7 and PG 36 are used for a very wide range of products such as paints, inks, coloring agents for various types of resin products, pigments for color filters of liquid crystals, and coloring of resins and other materials. Considering these applications and the concentrations of HCB in final products, it does not seem that the use of the final products would have a direct effect on human health, but the companies are confirming the effects of HCB taking the final applications into consideration.

It is difficult to immediately replace these pigments with alternative materials because their performance of weatherability and heat resistance are superior to those of other pigments.

2. HCB contamination level

Regarding the contents of residual by-product HCB in PG 7 and PG 36, in addition to the analytical data taken by manufacturers, importers, and users, the government has conducted analysis of samples collected from companies that had stocks of these pigments (see Annex 11 and Annex 12). According to the results of analysis, PG 7 contains HCB in the range of 0.54-220ppm and PG 36 contains HCB in the range of 0.32-11ppm.

In addition, in some cases, the analysis results provided by the companies differed from those obtained by the government. The following factors are thought to be the causes of the difference.

(1) Differences in the process used to extract HCB from the pigment

Although most of the companies and analytical laboratories extract HCB using liquid-liquid extraction with hexane after the pigment is dissolved in concentrated sulfuric acid, some analytical laboratories extract HCB by directly adding an organic solvent into the pigment and using ultrasonication. When ultrasonic extraction using an organic solvent is used, the analytical values tend to be lower compared with those obtained by sulfuric dissolution because HCB inside the pigment cannot be sufficiently extracted.

(2) Difference in the methods of quantitative determination

The results obtained by the absolute calibration curve method tend to be lower than those obtained by the internal standard method that uses internal standard substances. The reason for this is that the recovery rate cannot be corrected if the internal standard substance is not used, although no problem occurs when the recovery rate of HCB is high enough. When $^{13}C_6$-HCB is used as the internal standard substance, extra care must be taken in the setting of the measuring mass number because ions derived from HCB interfere with low-resolution GC/MS analysis. When $^{13}C_6$-HCB is used, there is a tendency for the results to differ from those obtained by the government using a high-resolution GC/MS, which is most probably caused by the ion interference described above.

(3) Low concentration of the sample

When the concentration of the sample is low, the magnitude of the difference from the results obtained by the government tends to increase. This seems to arise from the instability of the analysis due to inappropriate treatment of the intercept of calibration curve and the low sensitivity of the equipment used. When the concentration of the extracted solution is in the lowest concentration portion of the calibration curve or lower than the minimum end of the curve, it is necessary to reconsider the amount of sample and that of the aliquot.

Therefore, in consideration of the causes of analytical errors, to establish the BAT Level, it is necessary to employ a common analytical method for confirmation (see Section 9 described later).

3. Manufacturing method of phthalocyanine pigments

(1) Description of the manufacturing method

A crude raw material of blue pigment called Blue Crude (copper phthalocyanine crude) is produced first, then PG 7 is produced by chlorinating this compound and PG 36 is produced by chlorination and bromination. Some companies implement integrated manufacturing from the Blue Crude to the final pigment products of PG

7 or PG 36, and others purchase Blue Crude as the raw material for the manufacturing of PG 7 or PG 36.

(2) Manufacturing of Blue Crude

The manufacturing methods for Blue Crude are broadly classified into two groups as described below:

a) Urea method

A method in which Blue Crude is produced from phthalic anhydrride by reacting phthalic anhydride with urea and copper chloride. In the reaction process, Blue Crude is produced via intermediate products such as phthalimides.

b) Phthalodinitrile synthetic method

A method in which Blue Crude is produced by reacting phthalodinitrile with copper chloride.

(3) Chlorination, etc. of Blue Crude

When Blue Crude heated and melted is mixed with aluminum chloride, sodium chloride, etc., and chlorinated under heating, PG 7 is obtained; and PG 36 is produced by chlorination and bromination. The PG 7 and PG 36 produced in the above-mentioned process are pigmented through a final finishing process including size control. Detailed conditions of chlorination (chlorination and bromination for PG 36) and the finishing process (such as reaction temperature and time) differ from company to company.

4. Generation of by-product HCB in the manufacturing process for phthalocyanine pigments

The government conducted analysis of the samples of the raw material Blue Crude used for the production of PG 7 or PG 36, which were provided by manufacturers of PG 7, etc. to confirm the contamination level of HCB. The results showed that no HCB was detected in 44 samples out of total of 49 samples analyzed (minimum detection limit: 0.02ppm or 0.01ppm), and the amounts of HCB contained in all the remaining five samples were in the range below the minimum determination limit.

Data obtained by hearings with several companies show that there is little difference in HCB concentrations between the PG 7 and PG 36 immediately after the generation and those after the pigmenting process.

The above-mentioned fact indicates that the HCB contained in PG 7 and PG 36 is generated as a by-product when the Blue Crude is chlorinated. Furthermore, judging from the results of hearings with the companies, there seems to be the following two causes for the generation of by-product HCB in the chlorination process of Blue Crude:

(1) Chlorination of impurities contained in Blue Crude.
    HCB is generated by the chlorination of residual solvents (such as alkyl benzene) in Blue Crude that were used in the production of Blue Crude and unreacted raw materials (chemical substances that have aromatic rings, such as phthalic anhydride, phthalimide).

(2) Perchlorination of PG 7 and PG 36
    Generated PG 7 and PG 36 are partially decomposed by perchlorination so that HCB is finally generated.

According to the results of analysis conducted by several companies on the relationship between the elapsed time and the amount of generated HCB, some amount of HCB was detected even before the chlorine is introduced (i.e., when Blue Crude is mixed with aluminum chloride, and heated and melted). This fact indicates that by-product HCB generated by (1) (impurities in Blue Crude are chlorinated by aluminum chloride or other materials under the heated and melted state so that HCB is generated). It has been also reported that the amount of HCB contained in PG 7 varies depending on the kinds of impurities (residual solvents) in the raw material Blue Crude (details are described in Section 5. (1) later). This also supports the assumption that impurities in Blue Crude cause the generation of by-product HCB.

(2) is suggested by the fact obtained from the same above-mentioned analysis that HCB is suddenly generated close to the end-point of the chlorination reaction.

However, it is not clear which of (1) and (2) contributes more to the generation of by-product HCB in the manufacturing process for PG 7 or PG 36 because sufficient data are not available to make this judgment.

Comparison of the HCB concentrations in PG 7 and PG 36 produced in Japan indicates that the concentration in PG 36 tends to be lower than that of PG 7. The major reason for this is presumed to be that the amount of chlorine introduced in the manufacturing process for PG 36 is smaller than that introduced in the manufacturing process for PG 7 because bromination as well as chlorination is implemented for PG 36, and that when chlorination is implemented after bromination, impurities such as residual solvents are brominated first so the absolute amounts of impurities that can be converted to HCB by chlorination are reduced. However, details are not yet clear.

When the HCB concentrations in pigments (according to the results of sample analysis conducted by the government) are compared based on the difference in the manufacturing methods of raw material Blue Crude (see Section 3. (2) described above), PC 7 manufactured by using Blue Crude produced by the urea method contains a wide range of concentrations from several ppm to some 200ppm whereas PC 7 manufactured by using Blue Crude produced by the phthalodinitrile synthetic method contains only several ppm at most. In the case of PG 36, on the other hand, HCB concentration is about 10 ppm regardless of the method used for the production of the raw material Blue Crude. Thus, in order to reduce the HCB concentration in PG 7, it is effective to use Blue Crude produced by the phthalodinitrile synthetic method as the raw material compared with the Blue Crude produced by the urea method. As for PG 36, there is no difference in the HCB concentration between the methods for the preparation of Blue Crude.

5. HCB reduction measures in the manufacturing process of phthalocyanine pigments

For the reduction of HCB contained in PG 7 and PG 36, there are two main measures based on the mechanism of the generation of by-product HCB: 1) measures relating to the raw material Blue Crude and 2) measures in the manufacturing process of PG 7 and PG 36. In the case of PG 7, since the HCB content varies significantly depending on the methods used to manufacture Blue Crude (see Section 4 described above), the selection of the optimum manufacturing method for Blue Crude may be one of the alternatives for 1). The measures classified into 2) include a technology that suppresses the generation of by-product HCB in the chlorination process and a technology that removes the by-product HCB after the chlorination process.

(1) Measures relating to the raw material Blue Crude

a) Reduction in the amounts of impurities

Since one of the reasons for the generation of by-product HCB is the impurities contained in Blue Crude, the first measure to be taken is to use Blue Crude containing less impurity (use of high-purity Blue Crude). Usually the purity of Blue Crude is 96-98% and the impurities include reaction solvents for the synthesis of Blue Crude and residue of unreacted materials.

Numerous manufacturers have reported that the amounts of by-product HCB after the chlorination process decrease as the residual solvents decrease in the raw material Blue Crude (as the purity of Blue Crude increases). As a matter of fact, some companies position the reduction of impurities in Blue Crude or the procurement and use of high-purity Blue Crude as one of the measures for reducing by-product HCB.

On the other hand, some other companies have reported that no definite relationship between the purity of Blue Crude and the amounts of by-product HCB has been observed. Furthermore, the effect on the quality of products must be considered because there are reports that the use of high-purity Blue Crude causes problems in the pigmenting process and changes in hue.

b) Selection of the type of solvent

In addition to the purity of Blue Crude, it has been reported that the type of residual solvents in Blue Crude affects the amount of by-product HCB in PG 7 (see Table below). Although the reason for this is not clear, an effective approach is to use Blue Crude that has been produced using solvents that minimize the generation of by-product HCB as much as possible.

Table HCB concentration according to the type of residual solvents in the raw material Blue Crude

Raw material Blue Crude		HCB concentration after the chlorination (ppm)
Type of residual solvent	Purity of Blue Crude (%)	
Solvent A	96.7	25
Solvent B	97.8	27
Solvent C	97.5	30
Solvent D	97.7	70
Solvent E	97.7	96

Prepared by Secretariat based on information obtained from experiments (on a laboratory scale) conducted by a company

In order to implement the above-mentioned measures a) and b) relating to the impurities in Blue Crude, the options are to procure Blue Crude manufactured using high-purity Blue Crude or Blue Crude purified by such treatment as cleansing. Actual measures taken by the companies differ from company to company because they use their own procurement methods.

As described above, the purpose of measures relating to the impurities in Blue Crude is a technique basically to reduce the by-product HCB in PG 7 and PG 36. However, the effects vary depending on the differences in the manufacturing process of each company and the way Blue Crude is procured and quality of the product pigments are different. Therefore, it must be noted that the measures may not be applied across the board.

c) Change in the Blue Crude manufacturing method

As described in Section 4 above, when Blue Crude produced using the phthalodinitrile synthetic method is used, HCB concentration in PG 7 is only several ppm at most, which is apparently much lower than the HCB concentration in PG 7 derived from Blue Crude produced using the urea method. Although it is supposed that the reason for this is related to the amounts and types of impurities in Blue Crude (it is generally said that relatively pure Blue Crude is obtained by the phthalodinitrile synthetic method compared with the urea method), there are no specific data (quantitative data that compare the amounts and types of impurities in PG 7 produced by both methods) that confirm this assumption. A manufacturer of PG 7 who uses Blue Crude made by the phthalodinitrile synthetic method has pointed out that the main factor is the difference in the reaction temperature in the chlorination process (see item (2) a) described later). Thus, it is not necessarily clear whether the difference in the methods of producing Blue Crude is related to the HCB concentration in PG 7. However, in the reduction of HCB concentration in PG 7 from a technical viewpoint, optimization of the Blue Crude manufacturing method (the use of Blue Crude produced by the phthalodinitrile synthetic method) is a promising measure.

However, the results of hearings with the companies indicate that it is difficult to adopt the phthalodinitrile synthetic method across the board for the following reasons, and it seems to be difficult to establish the value as the BAT Level at this moment.

First, most of the manufacturers of PG 7 and PG 36 are using Blue Crude produced by the urea method. According the companies concerned, it is practically impossible for all the manufacturers, judging from the available supplies, to procure Blue Crude produced by the phthalodinitrile synthetic method.

Second, since the facilities used for both methods are so different that any change in the manufacturing method requires a large amount of investment, it is economically difficult to change the manufacturing method.

Third, since phthalodinitrile is specified as a Type II monitoring chemical (chemical substance which has low bio-accumulation but is persistent and possibly harmful in terms of its long-term toxicity in humans), it is necessary to carefully investigate before introducing this substance in large quantities as the raw material for Blue Crude.

(2) Reduction of by-product HCB in the chlorination process

It has been confirmed by multiple manufacturers that the generation of by-product HCB in the chlorination process of Blue Crude can be reduced by preventing excessive chlorination by changing the reaction temperature and the amount of chlorine introduced.

a) Temperature control

Multiple manufacturers have reported that reduction in the temperature of the chlorination process (melting temperature or reaction temperature) or appropriate temperature control contributes to the reduction in the generation of by-product HCB, and some of them actually adopt this method as a measure for reducing HCB.

On the other hand, some manufacturers have reported, based on production experiments in which the temperature was varied, that there was no clear relationship between the reaction temperature and the amount of by-product HCB. It has also been pointed out that reduction in reaction temperature generally leads to a longer reaction time resulting in higher cost and problems in production control.

b) Control of the amount of chlorine introduced

Information from several companies indicates that, in addition to temperature control, appropriate control of the amount of chlorine introduced (to limit the amount of chlorine introduced to the requisite minimum) is also effective in preventing excessive chlorination. As a matter of fact, numerous companies are implementing control of the amount of introduced chlorine.

On the other hand, one company controls the hue by changing the degree of chlorination. However, it is said that the HCB concentration does not change in accordance with the hue in the range of chlorine substitution corresponding to PG 7, which is between 13 and 15. There is another report that reduction in the time required for chlorination by increasing the amount of chlorine introduced per unit time, instead of decreasing the total amount of chlorine introduced, is effective in reducing the generation of by-product HCB.

Although details of manufacturing process differ from company to company (including the scale of facility) in this manner, it is nevertheless important to study and adopt the optimum amount of chlorine to be introduced in order to control by-product HCB.

(3) Reduction measures after the chlorination procedure

Several companies verified the removal of by-product HCB, on a laboratory scale, by washing PG 7 or PG 36 after the chlorination process using various types of solvents. The results showed that washing with some types of organic solvents brought about certain effects on the reduction of HCB. However, since the use of a large amount of new organic solvents is unfavorable from the viewpoints of worker safety, fire prevention, and effect on the environment, it is necessary to carefully investigate the appropriateness of this approach before it is actually adopted.

In the pigmenting process including size control, no company is studying the addition of a treatment process in order to reduce HCB by such means as washing because it is technically difficult and, moreover, such treatment has a much greater effect on the quality of the pigment.

6. The BAT level for HCB in phthalocyanine pigments

(1) Importance of establishing BAT Level

As described in Section 3 of Part I, the Three Ministries decided, as of April 2006, to study the BAT Level for phthalocianine pigments including the need to establish the BAT Level. After Committee deliberations based on the information obtained by the hearings, it was decided to promote the measures taken by the companies concerned by setting BAT Level for PG 7 and PG 36 if it is technically and economically possible to do so. The reasons for this decision are as follows:

a) At present, HCB concentrations vary depending on manufacturers and importers.

b) Unlike pigments derived from TCPA, by-product HCB is generated in the manufacturing process of these phthalocyanine pigments, and it is important to reduce the generation of HCB in the manufacturing process (that is, from the viewpoint of the generation of by-product HCB, phthalocyanine pigments are placed in the same position as TCPA, which is different from that of pigments derived from TCPA, such as SR 135).

c) Since the amounts of PG 7 and PG 36 manufactured and imported are much larger than those of pigments derived from TCPA, such as SR 135 and their applications are diverse, it is necessary to reduce the generation of by-product HCB in the manufacturing process of PG 7 and PG 36 as much as possible.

(2) BAT Level for PG 7

It is known that the difference in the manufacturing method of the raw material Blue Crude for PG 7 is related to the difference in HCB concentration, and the HCB concentration in PG 7 is in the order of several ppm when Blue Crude produced by the phthalodinitrile synthetic method is used while the HCB concentration is usually in the order of several tens of ppm (some samples contained more than 100ppm) when the urea method is used. However, it is not appropriate due to the conditions described in Section 4. item (1) c) above to consider the adoption of the phthalodinitrile synthetic method, which provides Blue Crude containing a lower concentration of HCB, as BAT (Best Available Technology).

Other effective measures for the reduction of by-product HCB concentration in PG 7 include, as described in Section 4 above: (i) measures relating to the impurities in the raw material Blue Crude (reduction in the amounts of impurities or optimization of the types of impurities), and (ii) measures taken in the chlorination process (appropriate control of temperature and/or the amount of chlorine introduced). Measures actually taken and the effects vary depending on individual companies.

Manufacturers who use the raw material Blue Crude produced by the urea method have investigated the optimum conditions relating (i) and (ii) described above, and voluntarily taken measures that have been proved to be effective in reducing HCB (mostly combining several technical measures). Progress in these investigations differs from company to company and some companies still have research subjects that will require further investigation. However, as a result of the above-mentioned nation-wide efforts, HCB concentrations of most of PG 7 supplied in Japan are 50ppm or less now. Furthermore, the information obtained from the hearings indicates that the concentration can be reduced to about 30ppm by most of the manufacturers and further reduction (to 20ppm or even 15ppm, for example) may be realized by some companies.

Based on the information described above, the realistic BAT Level at present is 50ppm on the premise that measures (i) and (ii) are taken (by the optimum combination according to the conditions of individual companies) when PG 7 is manufactured using Blue Crude produced by the urea method, and preferably, the value should be reduced to 30ppm in the future. However, since some companies are still at the study stage, it must be further discussed which of theses values is appropriate as the BAT Level of PG 7 taking the results of future investigations by the companies into consideration. For the time being, it is necessary for the manufacturers and importers of PG 7 to continue to make efforts to reduce the by-product HCB concentration by voluntary control and for the government to appropriately follow the implementation of measures by the companies.

(3) BAT Level for PG 36

According to the results of analysis by the government, there is not much difference in the HCB concentration in PG 36 depending on the difference of manufacturing method for used Blue Crude. The measures for the reduction of HCB concentration in PG 36 are basically the same as those for PG 7, and the two measures (combination of the two) described in (2) above are important.

The HCB concentration in PG 36 is low compared with that in PG 7 because bromination, as well as chlorination, is included in the manufacturing process of PG 36. In addition, as a result of the efforts of the manufacturers including the implementation of these two measures, the amount of by-product HCB concentration has been reduced to a significantly low level. Judging from such a situation, it is appropriate to set the BAT Level for PG 36 at 10ppm, which can be achieved by taking the reduction measures for HCB available to the companies (above-mentioned (2)(i) and (ii)). In addition, the value of 10ppm coincides with the BAT Level for SR 13 described in the First Report and that for other pigments derived from TCPA (excluding PY 138) proposed in Part II in this report.

7. Positioning of BAT level and future treatment

By-product class I specified chemical substances must be reduced as far as technically and economically possible. Therefore, after the implementation of the proposed BAT Level, the manufacture, import, or use of PG 7 and PG 36 with HCB concentrations higher than proposed BAT Level would not be permitted under CSCL.

Considering the time required for preparatory measures such as the securing of procurement of raw materials containing low level impurities (negotiation with the supplier of raw materials), it is appropriate to set a certain get-acquainted period before the entry into force of the proposed BTA Level. Therefore, the government must publish the proposed BAT Level and the schedule of enforcement as early as possible so that the companies concerned can take measures as quickly as possible. As for the BAT Level for PG 7, since a single value is yet to be proposed as described in Section 6. item (2) above, it is necessary for the Three Ministries to check the current status of the investigations being conducted by manufacturers of PG 7 consecutively and to take appropriate measures including consultation with the Committee as required.

Meanwhile, manufacturers and importers of PG 7 or PG 36 are expected to exert consistent efforts to supply PG 7 and PG 36 with as low as possible HCB concentration regardless of the proposed BAT Level. It is noted that the reduction of by-product HCB in PG 7 and PG 36 is particularly important because the amounts PG 7 and PG 36 produced and imported are much larger than those of pigments derived from TCPA including Solvent Red 135 and the applications are very diverse.

Therefore, it would be appropriate for the government to continue to strive to collect related information even after the implementation of the proposed BAT Level and to convene the Committee as required in order to consider and review the BAT Level on the basis of newly obtained information.

Furthermore, as for the users of PG 7 and PG 36 (those who color resins and other materials using proposed pigments, for example), full recognition that HCB is a class I specified chemical substance, are strongly expected to strive to procure and use pigments with an HCB concentration that is as low as possible.

8. Proper treatment of HCB removed in the manufacturing process for phthalocyanine pigments

When an HCB reduction measure such as the washing of PG 7 or PG 36 after the chlorination process is added to the manufacturing process of PG 7 or PG 36, there is concern that a small amount of HCB contained in the washing water may be discharged into the environment. It is also possible that the residues and filtrate after the reaction contain HCB. Therefore, it is essential for manufacturers of PG 7 and PG 36 to fully recognize this fact and appropriately manage and treat wastewater including the filtrate after the reaction is completed and, at the same time, adopts strict treatment so as to prevent workers engaged in the process from being exposed to HCB.

9. Analytical technique for HCB contained in phthalocyanine pigments

For the quantitative analysis of HCB contained in phthalocyanine pigments, a method with a quantitation limit that provides stable measurement of concentrations less than one-tenth (1ppm) of the BAT Level (10ppm for PG 36) must be adopted.
Since phthalocyanine pigments are insoluble, as in the case of pigments derived from TCPA, such as SR 135, to most of the organic solvents, the pigments do not dissolve in the Soxhlet extraction using toluene so that the HCB content tends to be estimated at a lower value because the internal HCB content is not extracted completely.

Judging from the above-mentioned discussion, it is appropriate for the analysis of HCB contained in phthalocyanine pigments (especially, PG 7 and PG 36) to adopt the analytical technique described in Part II Section 10, “Analytical technique for HCB contained in pigments derived from TCPA” (examples of the analysis of HCB content in phthalocyanine pigments are shown in Annex 13).

[Annex 1]

Committee meetings for the preparation of this report

Date	Meeting	Agenda
October 12 (Thursday)	13th meeting (5th plenary session)	Future policy for the investigation of the by-product HCB derived from substances other than TCPA and Solvent Red
November 10 (Friday)	14th meeting (9th WG session)	Hearing (Manufacturers and importers of other pigment derived from TCPA and phthalocyanine pigments
November 24 (Friday)	15th meeting (10thWG session)	
December 1 (Friday)	16th meeting (11thWG session)	
December 8 (Friday)	17th meeting (12thWG session)	
December 15 (Friday)	18th meeting (13thWG session)	
December 21 (Thursday)	19th meeting (14thWG session)	
February 2 (Friday)	20th meeting (6th plenary session)	Discussion on the report (draft)

List of Commission Member

Takashi Arimura	Senior Researcher, Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
Katsumi Uchiyama	Professor, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University
Haruhiro Okuda	Head, Division of Organic Chemistry, National Institute of Health Sciences
Ojima Yoshikazu	Professor, Faculty of Science and Technology, Tokyo University of Science
Takashi Kameya	Associate Professor, Graduate School of Environment and Information Sciences, Yokohama National University
Atsuo Kishimoto	Economist, Research Center for Chemical Risk Management, National Institute of Advanced Industrial Science and Technology (AIST)
Hidetoshi Kuramochi	Senior Researcher, Material Cycles System Engineering Section, Research Center for Material Cycles and Waste Management, National Institute for Environmental Studies
Shinichi Sakai	Professor, Environment Preservation Center, Kyoto University
Hiroaki Shiraishi	Director, Research Center for Environmental Risk, National Institute for Environmental Studies
Tomomichi Suzuki	Associate Professor, Faculty of Science and Technology, Tokyo University of Science
Makoto Misono	Professor Emeritus, the University of Tokyo (President, National Institute of Technology and Evaluation)

[Annex 2]

An Approach to By-product Specified Chemical Substances under CSCL concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc.

(Excerpt from Materials for the Chemical Products Council Held in April 1979)

(1) Concerning the Interpretation and Administration of CSCL concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc.

"(Abbrev.) Incidentally, the regulation of specified chemical substances under CSCL concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. is designed for the regulation of each substance categorized as a specified chemical substance, and the regulation is applicable even when such a substance is contained in other substances at the level where the industry terms an impurity.

The equity of statute of CSCL is the prevention of contamination by the release of specified chemical substances into the environment as products, and CSCL has been enacted bearing in mind that they are intentionally synthesized and sold. Accordingly, there should be a way of thinking that the regulation under CSCL is not applicable to substances that cannot be described as those being synthesized intentionally.

However, it is assumed that, taking particular care to curb the release of specified chemical substances into the open system is the minimum obligation imposed on chemical manufacturers, and that those who allow their products to contain the specified chemical substances, even as impure substances, beyond the technically and economically feasible levels are deemed to be manufacturing the specified chemical substances concerned through negligence of such duty of care, that, as such, these practices are recognized as the manufacture of specified chemical substances and made subject to the regulation under CSCL.

However, to recognize that the generation of even an infinitesimal quantity of impurities is manufacturing may conflict with socially accepted norms and such a quantity is naturally different from an amount that can be sought purely technically. Also, whether such a small quantity is regarded as sufficient level for user should be taken into consideration. (snip)"

[Annex 3]

Ideas about BAT under International Conventions and in Other Countries

1. International Conventions

○ Stockholm Convention on Persistent Organic Pollutants (2000)

Best available techniques (BAT) mean that "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for release limitations designed to prevent and, where that is not practicable, generally to reduce releases of chemicals listed in Part I of Annex C and their impact on the environment as a whole." (Stockholm Convention, Article 5 (f)(i)).

(Notes) Techniques: Include both methods to design, construct, maintain and operate as well as to abolish technologies and equipment in use,

Available: Operable by those who operate technologies and equipment in consideration of costs and benefits, and developed to the extent that related industry sectors can make use of under economically and technically feasible conditions, and

Best: Most effective in achieving the protection of the environment as a whole at a generally high level.

○ Convention of the Protection and Use of Transboundary Watercourses and International Lakes (Water Convention) (1992)

Best available technology (BAT) is taken to mean the latest stage of development of processes, facilities or of methods of operation which indicate the practical suitability of a particular measure for limiting discharges, emissions and waste.

2. European Union (EU)

○ Integrated Pollution Prevention and Control (IPPC) Directive

Best available techniques (BAT) mean "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole" (same as provisions in Article 5 (f) (i) of the Stockholm Convention in 1. above).

The IPPC Directive requires the application of BAT to facilities concerned. The EU prepares BAT Reference Documents (BREF) to provide the guidelines for competent authorities that issue operational permits. BREF include information on technologies that are deemed to the BAT level at the moment, and the authorities of EU member states use BREF as a reference in issuing operational permits to facilities concerned.

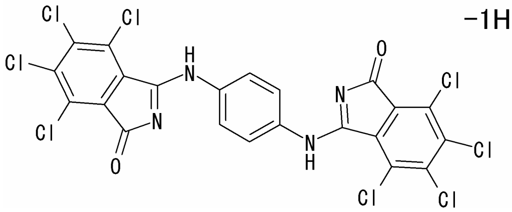
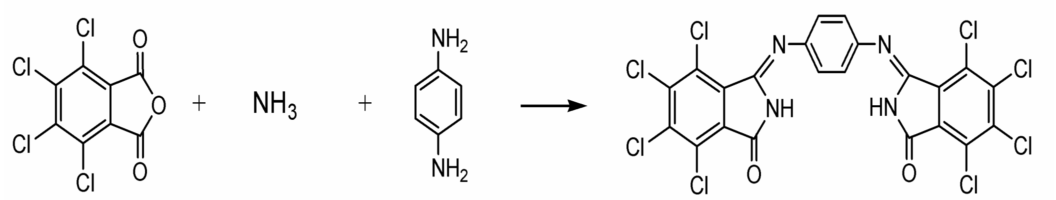
3. The United States

The United States has put into place a mechanism for reducing burdens on the environment through the introduction of better technologies in such areas as air pollution control and water pollution control. The mechanism is characterized by the establishment of emission standards for a variety of pollutants in each area from the standpoint of introducing better technologies.

(Examples) Water pollution control BAT (Best Available Technology)
Air pollution control MACT (Maximum Achievable Control Technology）
BACT (Best Available Control Technology）
Waste disposal BDAT (Best Demonstrated Available Technology）

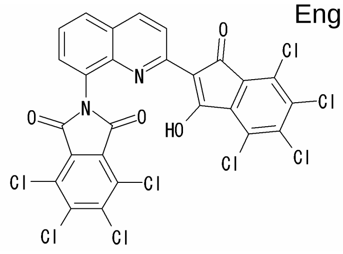
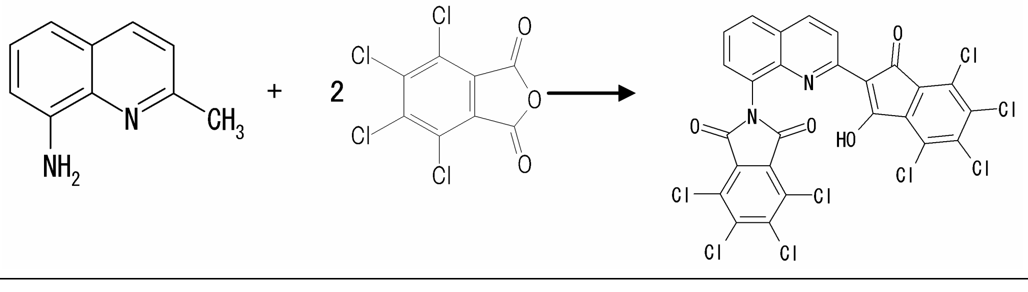
[Annex 4]

Description of Pigment Yellow 110

1	Structural formula			
	 English name: 3,3'-(1,4-phenylenediimino)bis[4,5,6,7-tetrachloro-1H-isoindol-1-one] CAS registration number: 5590-18-1 EINECS number: 226-999-5			
2	Composition formula	$C_{22}H_6Cl_8N_4O_2$		
3	Molecular weight	641.93		
4	Low concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture			
	Category	Existing chemicals		
	CSCL No.	5-3185		
	Existing list Official Gazette publication name	Pigment Yellow 110		
5	Physicochemical property			
	Appearance	Yellow powder (provided by manufacturer MSDS)		
	Density	–		
	Melting point	400°C (Beilstein)		
	Boiling point	–		
	Vapor pressure	–		
	Water solubility	–		
	LogPow	–		
6	Solubility in organic solvents (provided by manufacturer MSD)			
	Methanol, toluene	Insoluble		
7	Manufacturing methods			
				

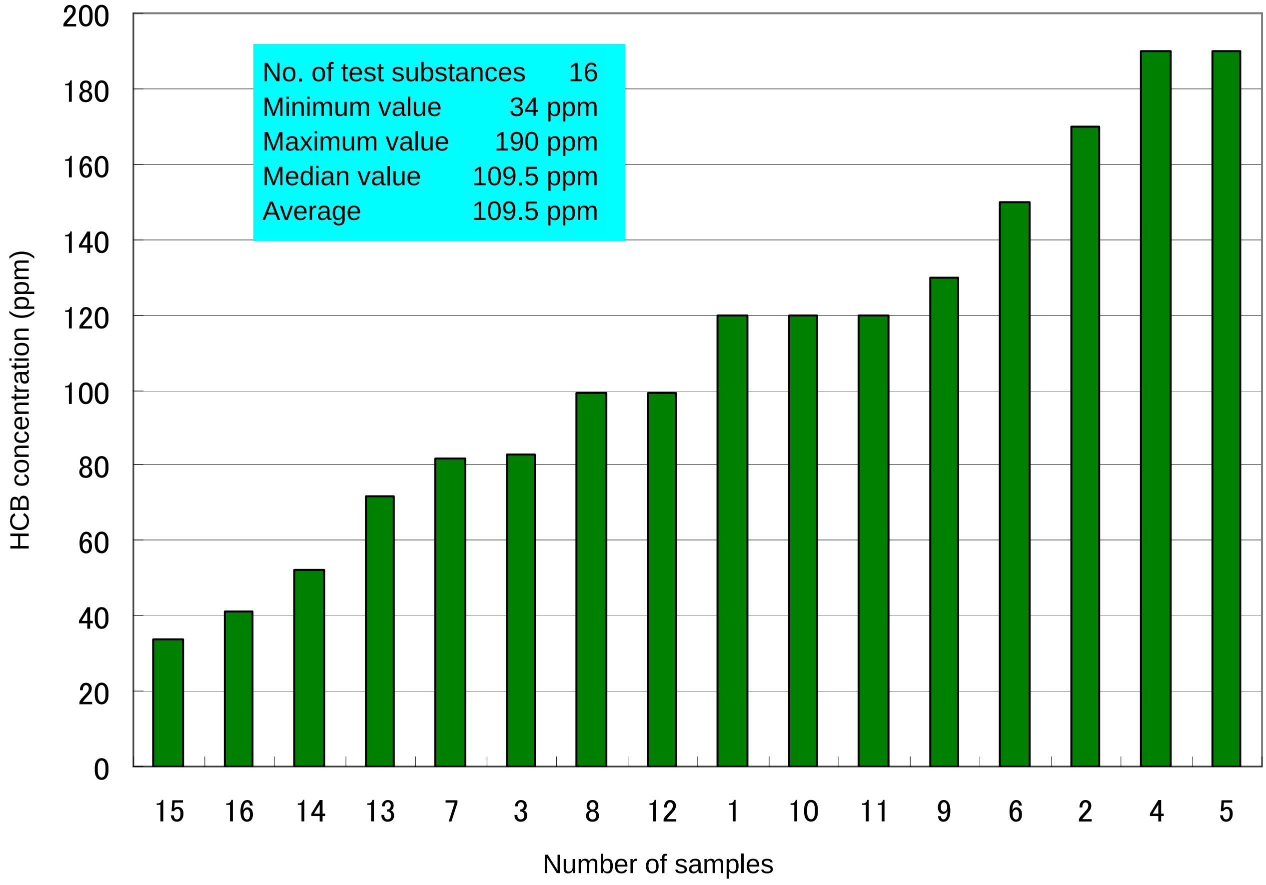
[Annex 5]

Description of Pigment Yellow 138

1	Structural formula			
	 English name: 3,4,5,6-tetrachloro-N-[2-(4,5,6,7-tetrachloro-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-8-quinolyl] phthalimide CAS registration number: 30125-47-4 EINECS number: 250-063-5			
2	Composition formula	$C_{26}H_6Cl_8N_2O_4$		
3	Molecular weight	693.97		
4	Low concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture			
	Category			
	CSCL No.	5-5281		
	Existing list Official Gazette publication name	2-(3-hydroxy-1-oxo-4,5,6,7-tetrachloro-2-indenyl)-8-(3,4,5,6-tetrachlorophthalimide) quinoline		
5	Physicochemical property			
	Appearance	Yellow powder (provided by manufacturer MSDS)		
	Density	–		
	Melting point	>200°C (provided by manufacturer MSDS)		
	Boiling point	–		
	Vapor pressure	–		
	Water solubility	–		
	LogPow	–		
6	Solubility in organic solvents			
	–	–		
7	Manufacturing methods			
	a) The product is obtained by reacting tetrachlorophthalic anhydride with 8-aminoquinaldine, then filtering and cleansing. 			

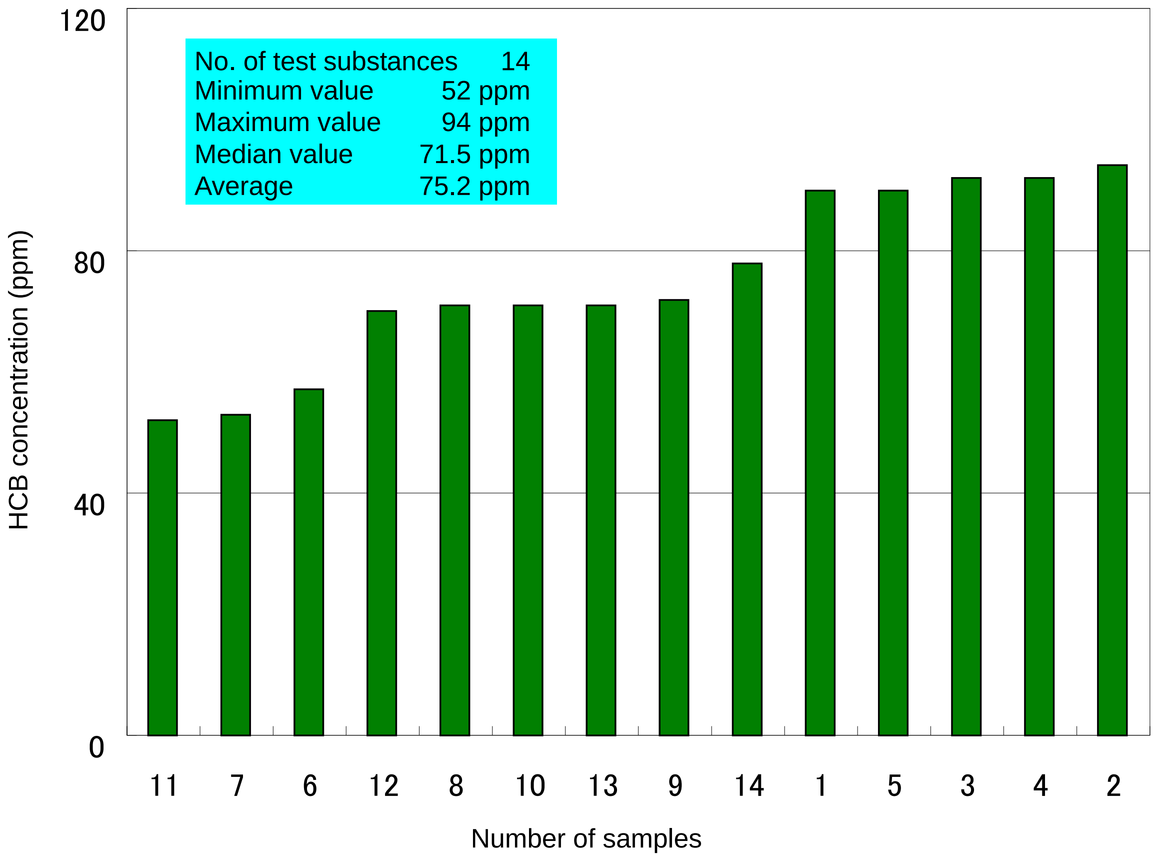
[Annex 6]

HCB concentration in the samples of Pigment Yellow 110 provided by the companies (results of analysis by the government)



[Annex 7]

HCB concentration in the samples of Pigment Yellow 138 provided by the companies (results of analysis by the government)



[Annex 8]

Example of Measurement of HCB content in other pigments derived from TCPA 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 pigments derived from TCPA (example of Pigment Yellow 138)

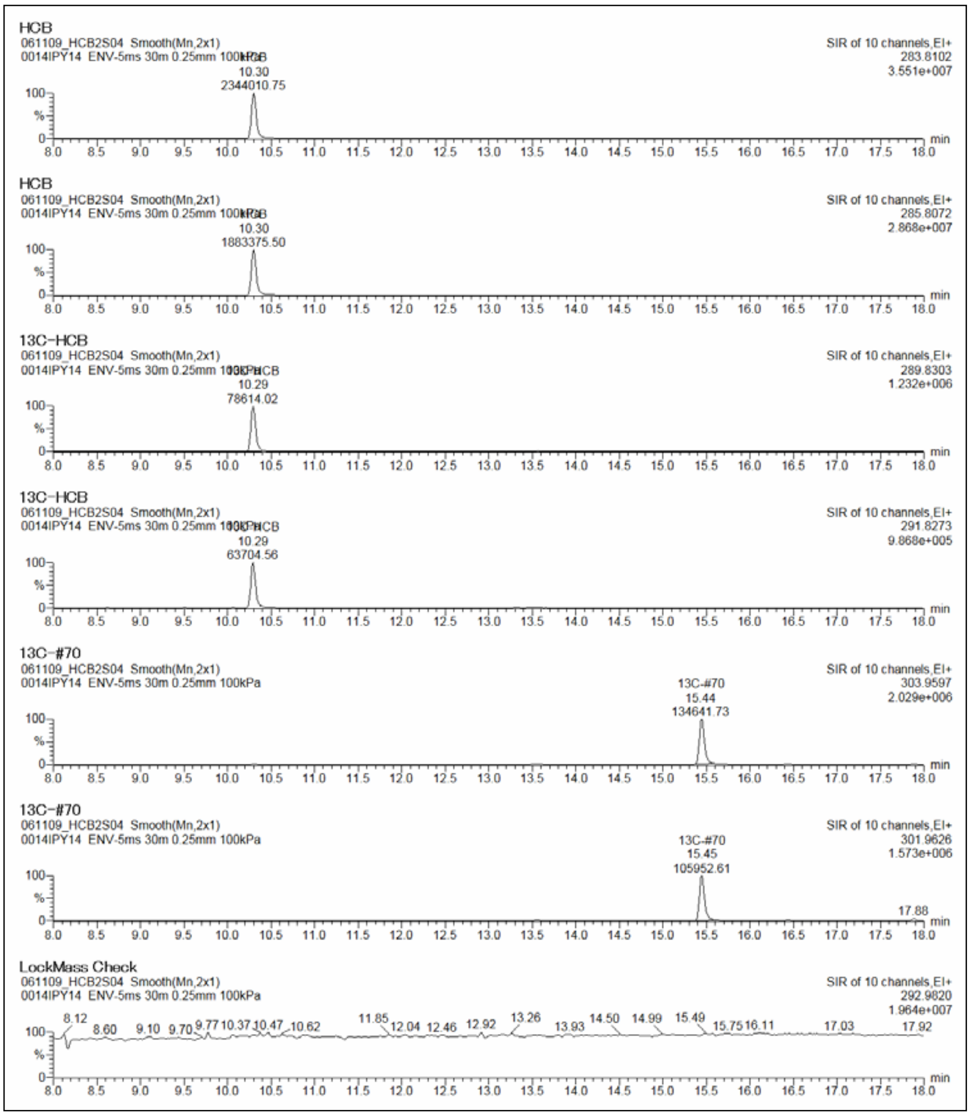


Figure1 SIM chromatograms of HCB analysis in the samples of Pigment Yellow 138

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

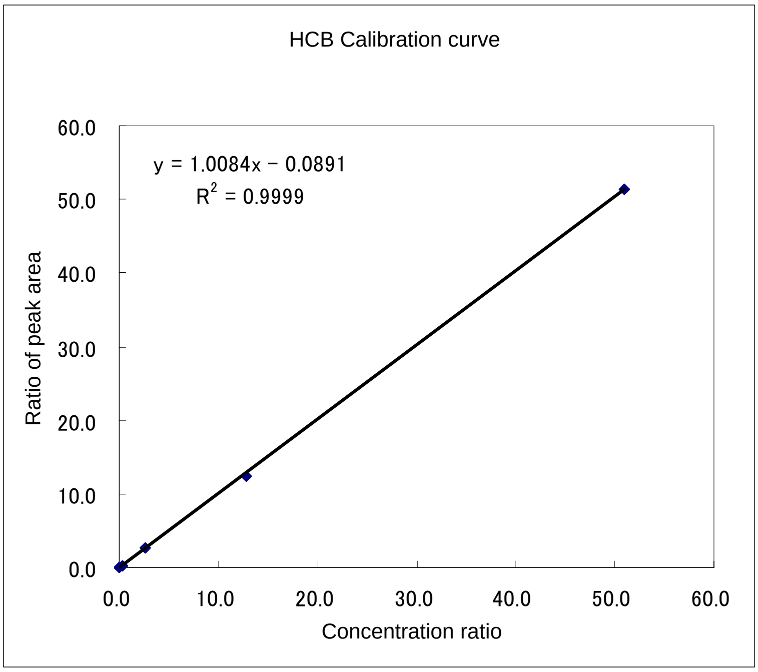


Figure 2 HCB calibration curve

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).

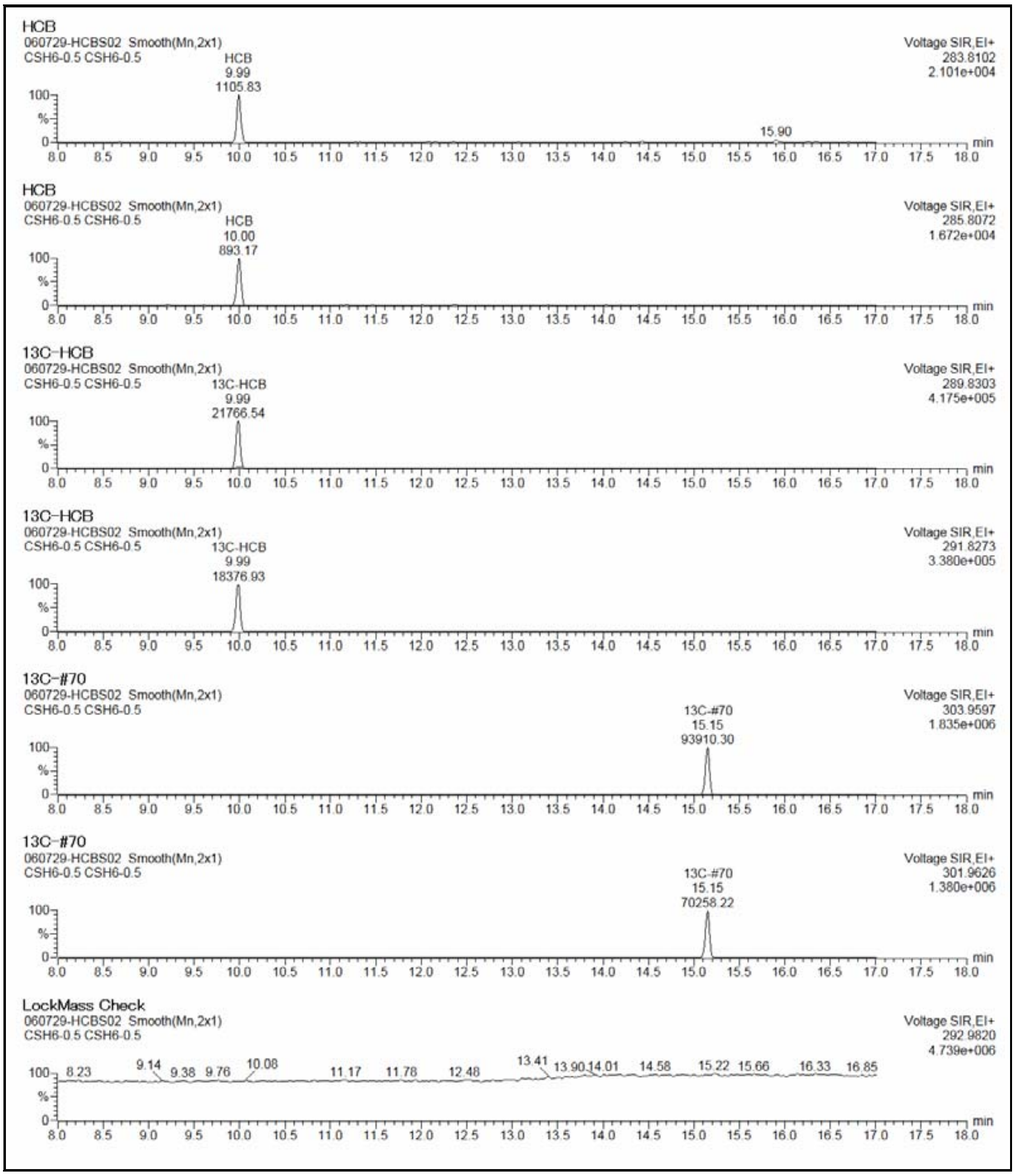


Figure 3 SIM chromatogram of the standard solution for the calibration curve with the lowest concentration

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)

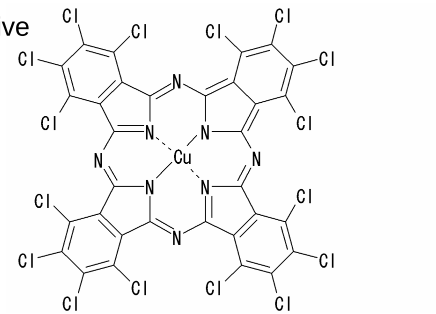
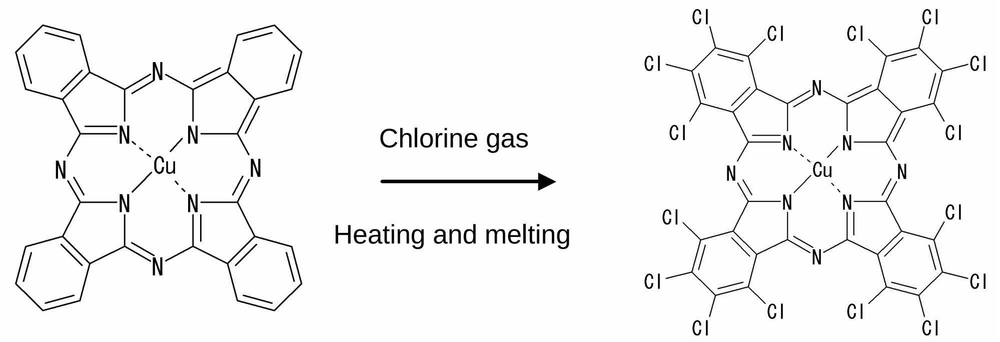
W: The quantity of the sample (g)

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

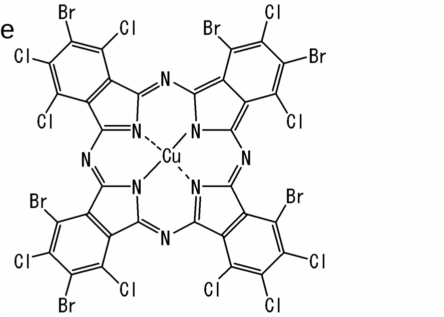
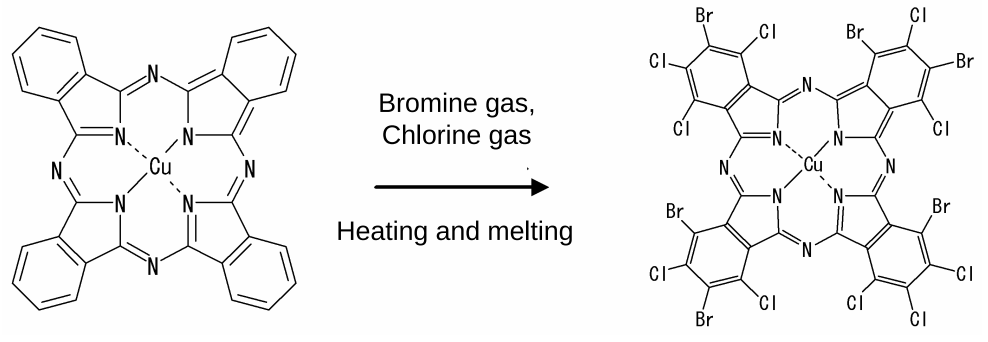
[Annex 9]

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 Pigment Green 7			

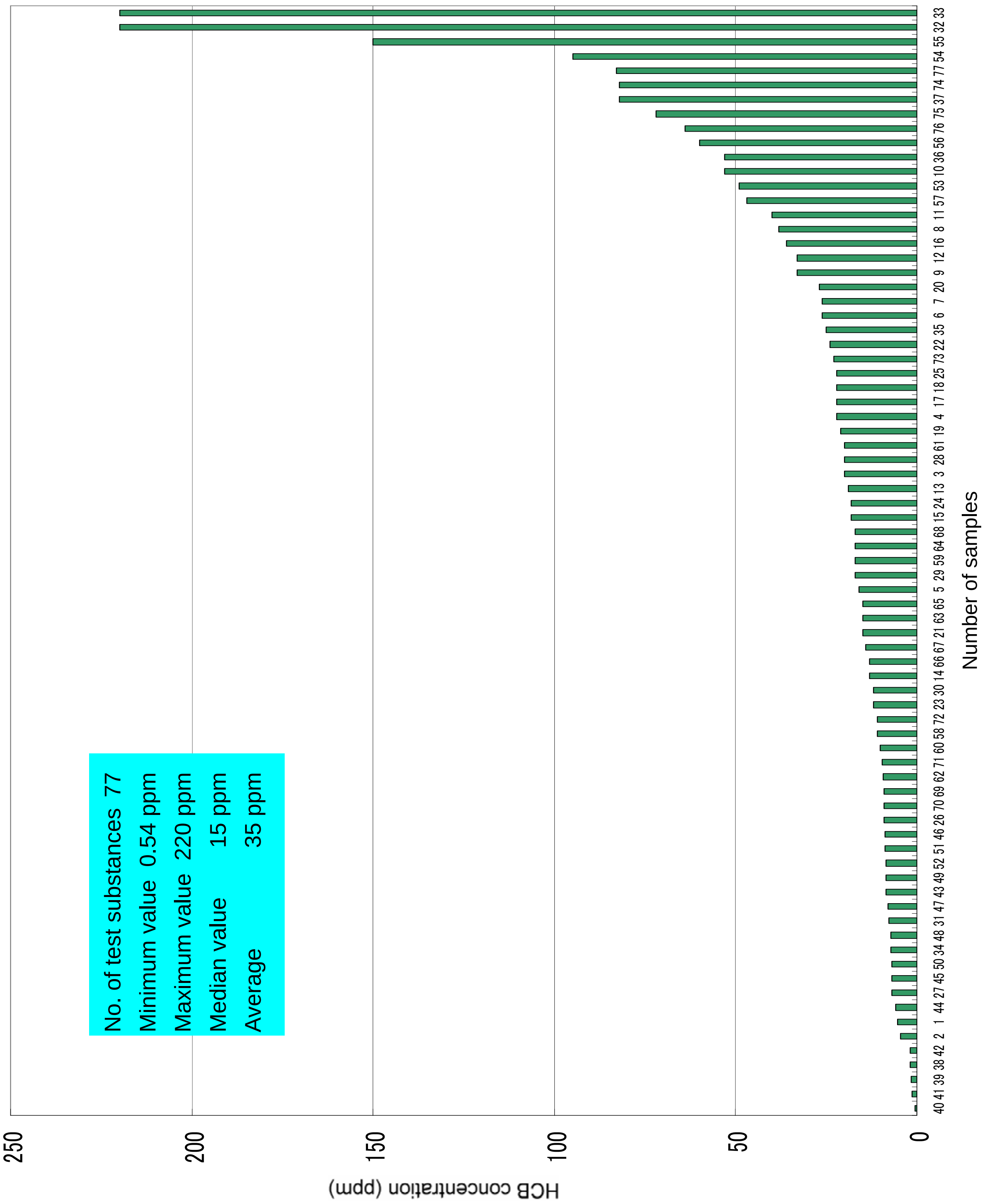
[Annex 10]

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 Pigment Green 36			

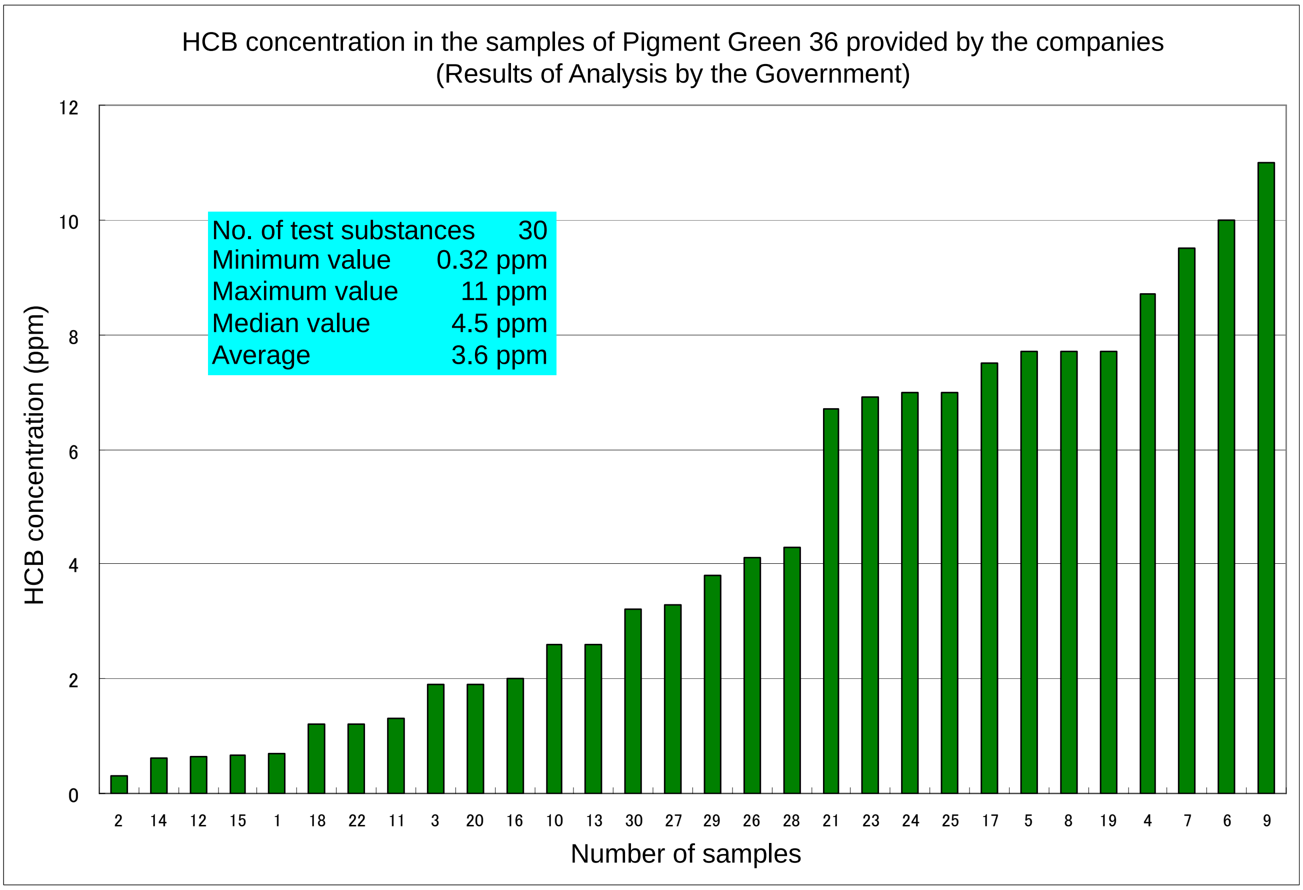
[Annex 11]

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)

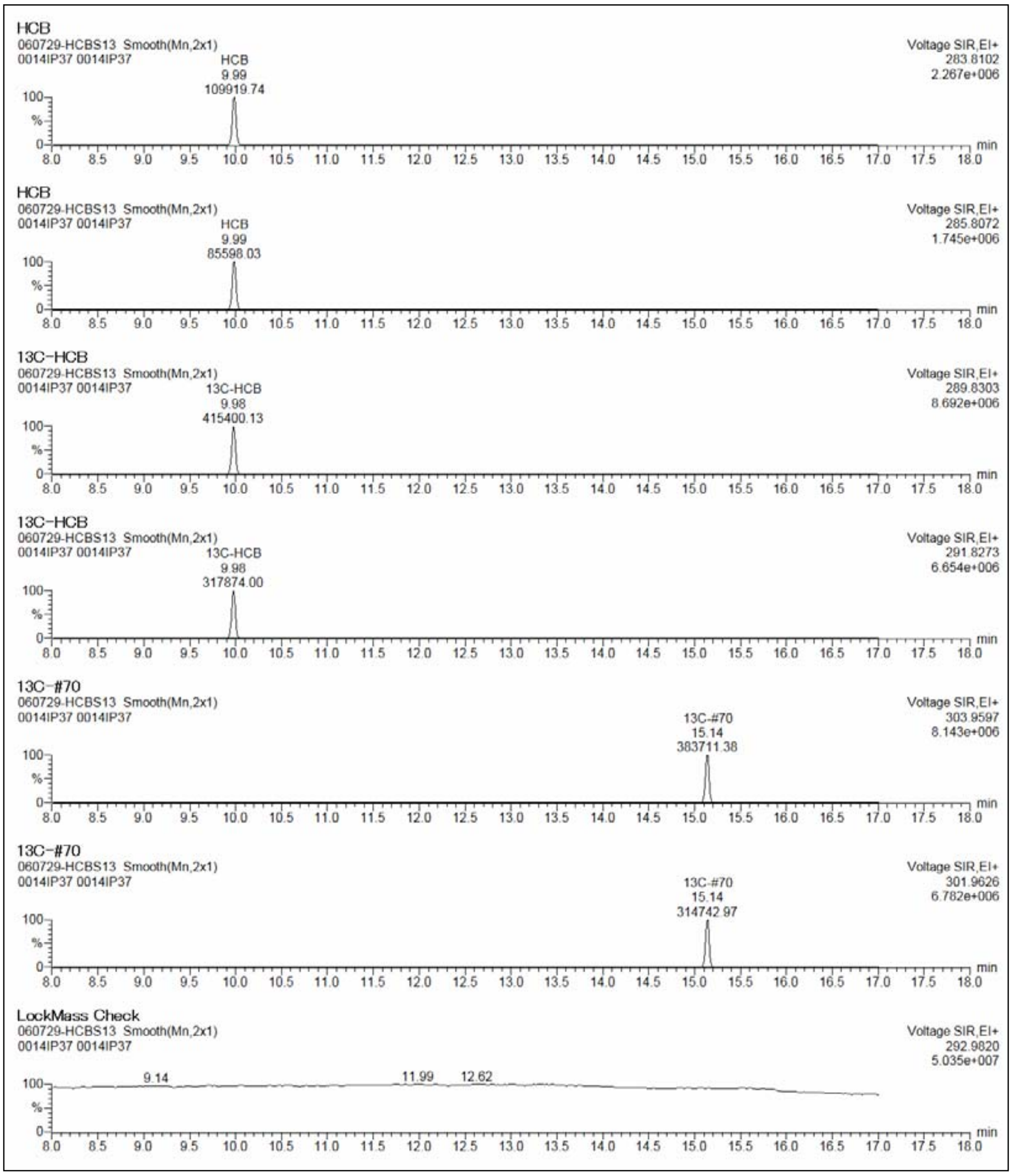


Figure1 SIM chromatograms of HCB analysis in the samples of Pigment Green 36

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).

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

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

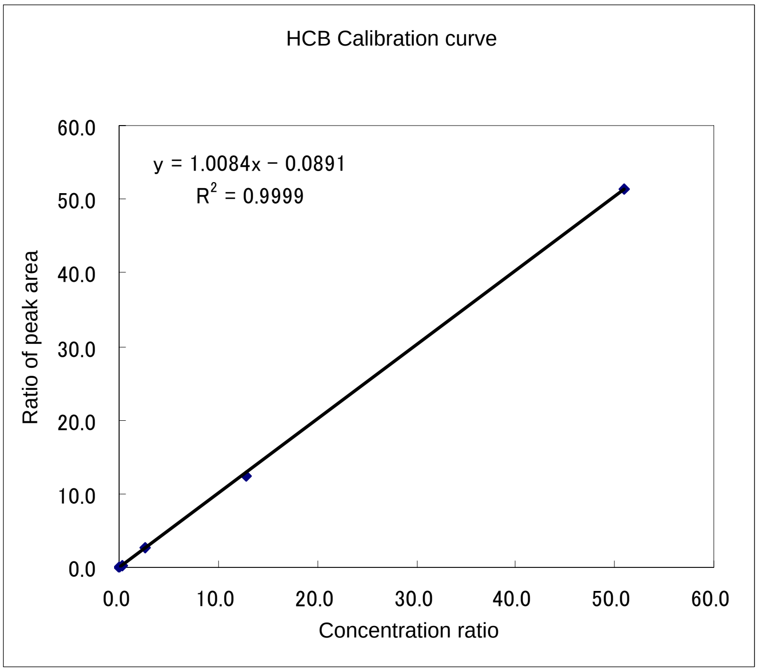


Figure 2 HCB calibration curve

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).

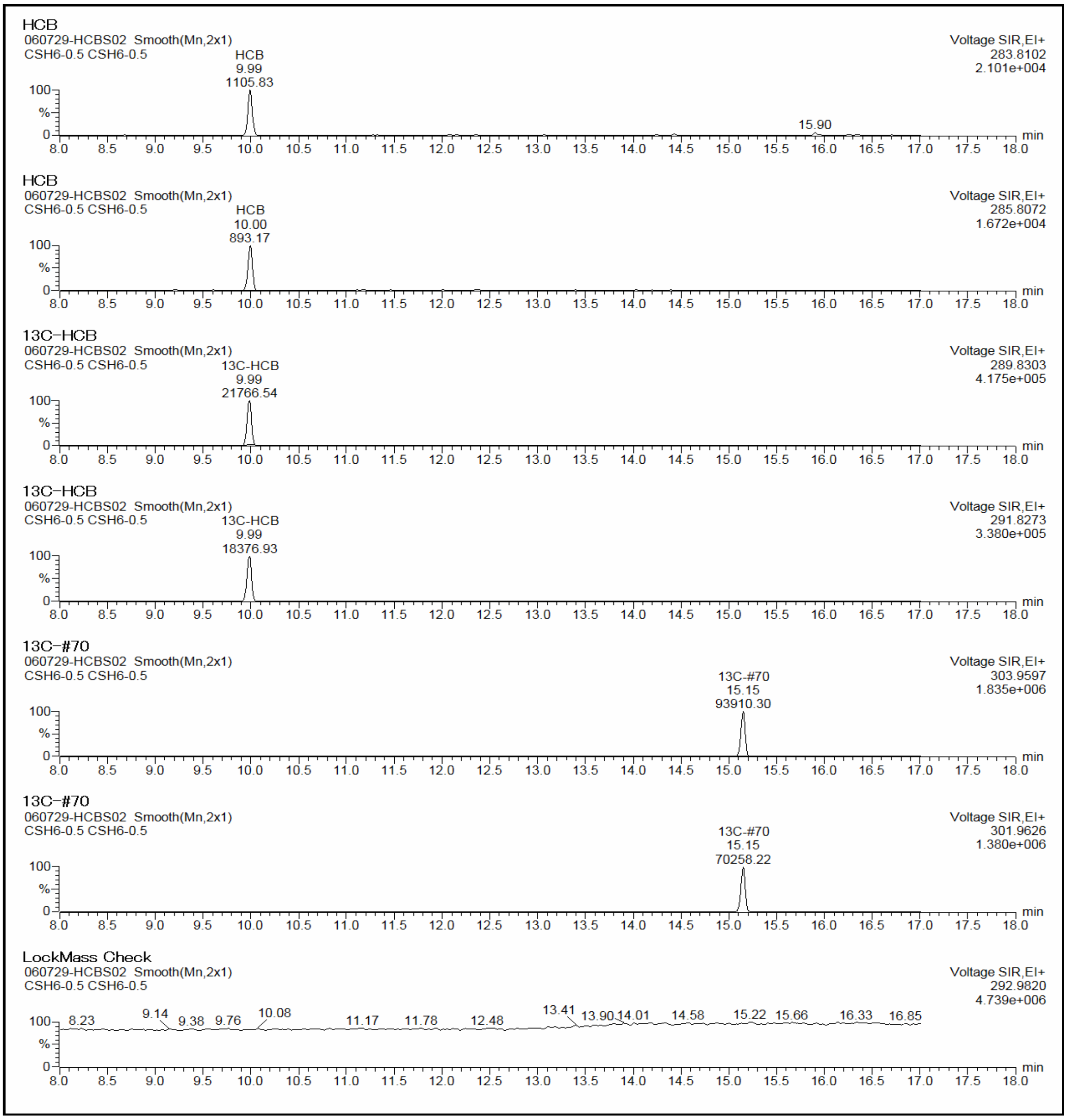


Figure 3 SIM chromatogram of the standard solution for the calibration curve with the lowest concentration

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