Report on BAT Levels concerning By-product HCB in TCPA and Solvent Red 135

(Provisional translation by the government)

November 2006

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

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

Executive Summary

I. Background

It was identified in Japan this February that HCB was unintentionally produced as a by-product at a significant level in the process of manufacturing tetrachlorophthalic anhydride (hereinafter referred to as “TCPA”, CAS No.117-08-8). The by-product HCB was contained not only in TCPA but also in its derivatives such as Solvent Red 135 (CAS No.20749-68-2). In Japan HCB is designated as one of the Class I Specified Chemicals of which production, import and use are prohibited under the Chemical Substance Control Law (hereinafter referred to as “CSCL”). Since it is important to reduce HCB, a Class I Specified Chemical, as a by-product in other chemical substances, as much as possible, CSCL requires its reduction by applying BAT (Best Available Technology/Techniques) for preventing its generation.

In April 2006, the Ministry of Health, Labour and Welfare (MHLW), the Ministry of Economy, Trade and Industry (METI) and the Ministry of the Environment (MOE) established an “Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product” to evaluate the technically and economically best feasible level (BAT level) for reduction of by-product HCB. In addition, the three Ministries required manufactures and importers of TCPA and its derivatives to take the most appropriate measures to reduce by-product HCB in these products as well as to manage and report the status of their production, import, sales and storage.

The committee comprising 11 academics met 13 times (including eight hearings from manufacturers and importers of TCPA and Solvent Red 135) and finalized its report on November 9, 2006.

II. The BAT Level for TCPA

1. Outline of TCPA

a) Usage: Raw material of dyestuffs and pigments such as Solvent Red 135

b) Amount of use in Japan: about 30 tons (in 2005)

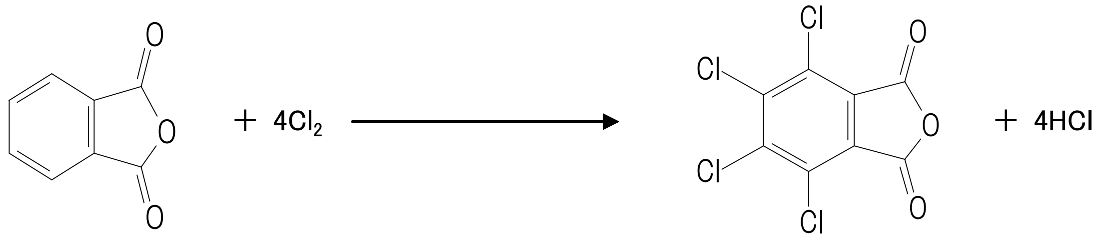
c) HCB contamination level: 110 – 3000ppm (according to the result of 60 samples analyzed by the government)

2. Manufacturing process of TCPA

There are two manufacturing methods as follows:

a) Gas phase method: This is a method of manufacturing TCPA by reacting phthalic anhydride with chlorine gas in the gas phase. It is said that this will generate HCB as a by-product more than in the liquid phase method, because the reaction temperature is high.

b) Liquid phase method: This is a method of manufacturing TCPA by reacting phthalic anhydride with chlorine gas in the liquid phase. The reaction solvent is fuming sulfuric acid or chlorosulfonic acid. TCPA has been manufactured mainly by the liquid phase method in Japan.



Phthalic anhydride TCPA

3. HCB Reduction Measures in TCPA

(1) Mechanism of Generation of HCB as a By-product

It is believed that the high temperature through the heat reaction generated by chlorinating phthalic anhydride would cause decarboxilation from TCPA or phthalic anhydride, which would generate HCB with further chlorination.

(2) Technology to Reduce By-product HCB in Manufacturing Process of TCPA

According to publicly available information in patent applications, temperature control to prevent the generation of high temperatures, and chlorination control to avoid excessive chlorination can reduce by-product HCB to a level of several hundred ppm (less than 200ppm is sometimes possible). The TCPA manufacturer who applied for this patent actually maintained a low level of by-product HCB in TCPA by adopting these operations at the factory level about 10 years ago. The data provided by this manufacturer shows that the HCB contamination level in TCPA was significantly decreased by the control of temperature and chlorination; from 1200 – 2100ppm (before the adoption of measures) to 500 – 900ppm (after adoption).

(3) Technology to Reduce By-product HCB after Manufacturing TCPA

By-product HCB can be reduced by recrystallization refinement using an organic solvent. A few manufacturers sell “high-grade TCPA” that contains less HCB than usual (e.g. less than 500ppm, or even less than 100ppm), and they say that it is produced by using recrystallization refinement. According to one TCPA manufacturer, the first recrystallization using a certain kind of organic solvent can reduce by-product HCB level in TCPA to 200ppm, while the second recrystallization can reduce it to 80ppm, and the third can reduce it to 40ppm. In a laboratory experiment conducted by the Chemicals Evaluation and Research Institutes, Japan (CERI) confirmed that recrystallization refinement using this organic solvent is quite effective by achieving a 65% reduction of HCB by a one-time refinement process.

Other manufacturers and importers of TCPA have also examined how to reduce by-product HCB by recrystallization refinement using other organic solvents. In a laboratory basis, it has been revealed that some kinds of organic solvents are more effective than the type actually introduced, showing more than 80% HCB reduction. These methods, however, are not desirable since they can lead to large increases in costs, and cause negative impacts on the environment and worker health because they make use of huge volumes of organic solvents.

4. The BAT Level for TCPA

Taking the above technical information into consideration, TCPA manufacturers can reduce by-product HCB to at least 200ppm by a combination of temperature and chlorination control and one-time recrystallization refinement. (Several hundred ppm is achieved by temperature and chlorination control, and then recrystallization refinement can reduce it further to less than 200ppm.) These techniques are both available at the current technical level of TCPA manufacturers.

According to the hearing in the Committee, it is estimated that one-time recrystallization would add about 25-40% to the TCPA price, which would be economically feasible for TCPA users.

Therefore, it is concluded that "200ppm" is appropriate as the BAT level for TCPA.

III. The BAT Level for Solvent Red 135

1. Outline of Solvent Red 135

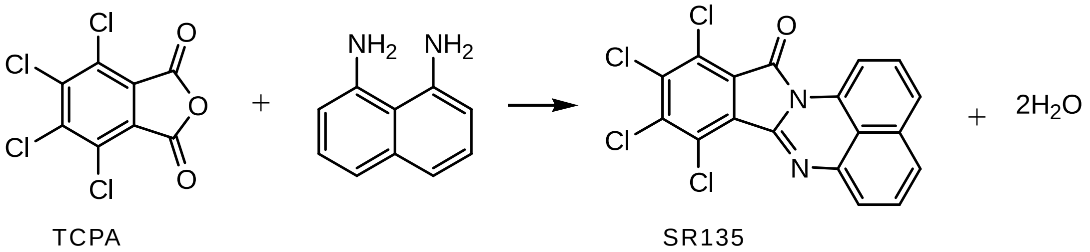
a) Usage: Pigments for plastics mainly used as auto parts (e.g., taillight covers) and electrical products

b) Amount of use in Japan: about 60 tons (in 2005, according to the results of the hearing)

c) HCB contaminant level: 0.084 – 310ppm (according to the results of 38 samples analyzed by the government)

2. Manufacturing Process of Solvent Red 135

Solvent Red 135 is manufactured by reacting TCPA with 1,8-naphthylenediamine in a reaction solvent. The reaction product turns to Solvent Red 135 through a process of cooling down, rinsing and drying. The detail of the process (e.g. kind of reaction solvent, condition of the reaction and the way of rinsing) depends on the manufacturer. As for reaction solvents, one TCPA maker uses water and the others have adopted organic solvents.



3. HCB Reduction Measures in SR135

(1) Mechanism of Generation of HCB as a By-product

It is found that by-product HCB in Solvent Red 135 is the result of a residue in raw TCPA, because additional chlorination does not occur in the manufacturing process of Solvent Red 135.

(2) Technology to Reduce By-product HCB in the Manufacturing Process of TCPA

If the organic substances are used as a reaction solvent, a large amount of by-product HCB is dissolved in the solvent in the process of manufacturing SR135. As a result, the manufacturing process using organic reaction solvent itself is an effective measure to reduce the by-product HCB level in Solvent Red 135. (On the other hand, Solvent Red 135 produced in water shows a relatively high concentration level of HCB.) According to the analysis of Solvent Red 135 manufactured in Japan, there is a proportional relation between the volume of HCB contained in TCPA and that in Solvent Red 135, and the concentration of HCB contained in Solvent Red 135 is usually several percent (3.3% at the maximum of available data) of that in TCPA.

(3) Technology to Reduce By-product HCB after Manufacturing SR135

One Solvent Red 135 manufacturer has tried to reduce contaminant HCB by enhancing rinse of reaction product at the factory level. Another maker also conducted a laboratory experiment of cleaning up Solvent Red 135 with several organic solvents. The results of these efforts, however, show that cleaning up

Solvent Red 135 after reaction is not an effective way to reduce by-product HCB.

4. The BAT Level for Solvent Red 135

Since HCB contained in Solvent Red 135 is a residue in material TCPA, reducing by-product HCB in TCPA as much as possible is the most important and effective measure to reduce by-product HCB in Solvent Red 135. Based on the relationship between HCB concentration in TCPA and that in Solvent Red 135, if TCPA contains less than 200ppm HCB, i.e. the BAT level proposed above, the concentration of HCB in Solvent Red 135 would be the order of several ppm. (Although there is no available data that shows how much HCB is actually contained in Solvent Red 135 if TCPA with 200ppm HCB is used, it is not likely that the HCB concentration in Solvent Red 135 is higher than 10ppm, 5% of that in TCPA.)

Therefore, it is concluded that "10ppm" is appropriate as the BAT level for Solvent Red 135.

IV. Implementation of the BAT level under CSCL

After these BAT levels are enforced in regard to the threshold value of by-product HCB under CSCL, the manufacture/import of TCPA or Solvent Red 135 containing HCB more than the BAT levels is deemed to be the manufacture/import of HCB under CSCL.

Since all TCPA sold in Japan is imported at present, the prompt enforcement of these BAT levels may influence the stable supply of TCPA and Solvent Red 135. Hence, the government should set an adequate period* before the entry into force of the BAT levels.

Part I Background of the Study

1. Details of the Case of By-product HCB

(1) Revelation of Production and Import

On February 17, a company reported that Tetrachlorophthalic anhydride (hereafter referred to as "TCPA," CSCL No. 3-1423, CAS No. 117-08-8) it had been importing contained some 1000-2000ppm (0.1-0.2%) of Hexachlorobenzene (hereafter referred to as "HCB," a Class I Specified Chemical,[1] CSCL No. 3-76, CAS No. 118-74-1).

Subsequent investigation by the Ministry of Health, Labour and Welfare, the Ministry of Economy, Trade and Industry, and the Ministry of the Environment (hereinafter referred to as "the three Ministries") confirmed that HCB was contained in TCPA produced by multiple companies and that TCPA containing HCB had been imported by multiple companies.

The companies handling TCPA confirmed that it contained HCB and voluntarily suspended shipments of TCPA. Detailed investigations revealed that HCB had been generated as a by-product in the synthesis process of TCPA.

(2) Investigation into the Actual Status of TCPA Use

On February 24, the three Ministries required domestic companies that produce chemical substances using TCPA to suspend use of TCPA, and asked the companies to report to them about HCB concentrations in their products and to suspend the shipment of the products pending further confirmation. The three Ministries also sought the companies' cooperation in an investigation into the actual status of the use of TCPA.

As a result, it was found that TCPA is mainly used as a raw material for dyes and pigments to color resins and for some paints, and that dyes and pigments (Solvent Red 135, etc.) produced using TCPA also contain HCB. As for Solvent Red 135, in particular, it was revealed that a variety of products are being manufactured using resins colored by the pigment. Judging from the uses of TCPA confirmed so far and the concentration levels of impurity HCB in end products, the use of end 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.

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[1] Class I specified chemicals under CSCL concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. are subject to a license system for manufacture and import (effectively prohibited) as well as to regulations including the ban on the use other than for specific purposes. At present, a total of 15 substances are designated as Class I specified chemicals. Of them, the manufacture, import, export and use of 12 substances are prohibited, in principle, under the Stockholm Convention on Persistent Organic Pollutants (POPs Convention).

Since March 1, companies that have been checked by the three Ministries regarding the content of HCB in products manufactured using TCPA as well as the possibility to release of HCB into the environment in view of the uses of those products have resumed shipments of products held in stock.

2. Basic Approach to Specified Chemical Substances as By-products

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 1 and Annex 2 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.

3. Establishment of the Assessment Committee

The investigation by the three Ministries found that, concerning the generation of HCB in the synthesis process of TCPA and HCB contained in Solvent Red 135 in this case, it is difficult to achieve the reduction of HCB concentration to the BAT level only through efforts on the part of individual manufacturers and importers based on the duty of care.

Globally, the manufacture of TCPA is oligopolistic (for that matter, a single manufacturer dwarfs all other producers to create a near-monopoly) and the absence of competition has resulted in little effort to reduce HCB concentration to a technically and economically feasible level, with the BAT level remaining unknown at this moment.

As for Solvent Red 135, individual manufacturers may have been exerting efforts to reduce HCB concentration, but the actual HCB concentration differs significantly among manufacturers, highlighting the reality that HCB concentration does not converge with the BAT level naturally through efforts on the part of individual manufacturers alone, with the BAT level also remaining unknown at that moment.

Also, as described later, there is no alternative substance to Solvent Red 135 in terms of maintaining the performance of end products, making it difficult in the foreseeable future to reduce by-product HCB through the promotion of substitution.

Consequently, the three Ministries decided on the prompt establishment of an assessment committee of experts to study issues related to TCPA and Solvent Red 135 and proceed with control over them based on the Best Available Technology/Techniques (BAT) approach. At the same time, pending the establishment and application of the BAT level, the three Ministries decided to ask manufacturers and importers of TCPA and Solvent Red 135 to exert maximum possible efforts toward the reduction of HCB concentration, and also instructed them to ensure tight control over, and to report to the three Ministries about the manufacture, import, marketing, storage, etc., of TCPA and Solvent Red 135.

On March 17, the three Ministries notified the parties concerned of the above-mentioned policy and also made it public together with developments surrounding this particular case. After the announcement of the policy, several manufacturers and importers of TCPA and Solvent Red 135 informed the three Ministries of their self-monitoring and control efforts pending the establishment and application of the BAT level, with the subsequent resumption of shipments of the products.

The Assessment Committee held its first meeting on April 7, in which the Secretariat of the Committee briefed its members on the developments concerning the case, and the members endorsed the Committee's establishment and measures to proceed with the study (see Annex 3). Subsequently, the Assessment Committee met eight times to conduct hearings with manufacturers and importers of TCPA and Solvent Red 135 and discussed matters concerning the BAT level on the basis of information gathered through the hearings (see Annex 4).

The establishment of the BAT level requires the study of both the technology for environmental protection and economic aspects. The technology for environmental protection refers to a range of technologies that can reduce by-product HCB concentration in the chemical substances such as TCPA and Solvent Red 135 supplied by companies. The criteria for the study from the economic aspect are whether technologies can be utilized under normal economic conditions. In order to make an assessment of these matters, the Committee gathered (1) information on TCPA and Solvent Red 135 (uses, manufacturers, manufacturing costs, actual selling prices, available supplies, substitutability by other substances, etc.), (2) information on manufacturing technologies (materials, processes, facilities, operational methods, and maintenance, etc.), and (3) information on analytical techniques and by-product HCB concentration in the chemical substances supplied, through hearings with manufacturers and importers of these substances, and then considered the BAT level.

This report put together the results of the study by the Assessment Committee, and discusses the BAT level for TCPA in Part II and the BAT level for Solvent Red 135 in Part III, respectively.

Part II The BAT Level for TCPA

1. Description of TCPA

The name, structural formula, and physicochemical property of TCPA are described in Annex 5. Domestic shipments of TCPA amounted to some 30 tons in 2005. [2]

TCPA is mainly used as raw material for dyes and pigments such as Solvent Red 135, and is related to the manufacture of a very broad array of products through the coloring of a variety of resins. For example, Solvent Red 135 is used worldwide as the red colorant for automobile tail lamps, and in many cases, it is difficult to replace it with other materials, partly because there are no other materials that can replace its weather resistance (light resistance) attributes in outdoor use. On the other hand, TCPA, which had been in use as painting material, was replaced by alternative materials immediately after it was identified as containing by-product HCB, and thus it is no longer in use.

2. HCB Contamination Level

As for the concentration of by-product HCB in TCPA, in addition to the analysis results provided by manufacturers, importers, and users, the government conducted analysis of samples collected from companies that had TCPA stocks (see Annex 6). According to the analysis, 110-3,000ppm of HCB (one-millionth (mg/kg) on a weight basis) was found in 60 specimens obtained by the government.

Since the analysis result of the concentration of HCB from the same production lot sometimes varied depending on the testing organization, it seems appropriate to present a certain unified analysis method to confirm the contamination level when the BAT level is determined (see Section 10 to be described later).

3. Manufacturing Method of TCPA

There are two manufacturing methods of TCPA: the gas phase method where phthalic anhydride and chlorine gas are used for the gas phase reaction, and the liquid phase method where phthalic anhydride and chlorine gas are used for the liquid phase reaction with fuming sulfuric acid or chlorosulfonic acid used as a reaction solvent. The gas phase method for manufacturing TCPA is said to produce a relatively larger amount of HCB than the liquid phase method because it has high reaction temperature and, as such, the condition of the reaction is very severe. It is

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[2] The amount is the sum of shipments reported by companies at the hearings in the committee meeting.

known that there have been several domestic TCPA manufacturers and all of them adopted the liquid phase method for manufacturing TCPA.

4. By-product HCB Concentration by Manufacturers

The average HCB contamination level in TCPA of one manufacturer was 2,300ppm (n=3), while those of other manufacturers were 1,100ppm (n=25) and 790ppm (n=20). [3]

Even when the same manufacturing method was used, the HCB contamination level significantly varied depending on the manufacturer. Although some TCPA showed low HCB concentration at 110ppm, there were no clear confirmed reasons for explaining these differences.

HCB Concentration in TCPA by Manufacturers

Manufacturer	HCB content
Company A	550～2,100ppm (n=25) Average 1,123ppm
Company B	1800～2,800ppm (n=3) Average 2,333ppm
Company C	110～1,700ppm (n=20) Average 785ppm
Company D	1200～3,000ppm (n=2) Average 2,100ppm
Company E	300～880ppm (n=5) Average 630ppm

Source: Analysis results conducted by the Japanese government.

5. HCB Reduction Measures in the TCPA Manufacturing Process

While the mechanism of HCB being produced as a by-product in the manufacture of TCPA has yet to be clarified, it is believed that the high temperature through the heat reaction generated by chlorinating phthalic anhydride causes decarboxilation from TCPA or phthalic anhydride, which generates HCB with further chlorination.

All manufacturers focused only on the HCB concentration of TCPA and had no data about the status of the HCB concentration in the TCPA manufacturing process. However, one company, in its filing of a patent application, identified key points in

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[3] Analysis conducted by the Japanese government. See Annex 6.

the reduction of the HCB content and showed some quantitative experimental data. The application for a patent was turned down and the contents of the application have been made public. Consequently, the technology described below can be used broadly and are not limited to use by the original applicant. Also, the technology in this patent application for the reduction of by-product HCB was examined on a scale close to that of a real manufacturing plant. The published information about the patent application cited the following three points as ways to reduce the production of HCB:

(a) Control the reaction temperature to keep it from rising excessively (while cooling, the reaction does not proceed if the temperature is lowered excessively)

(b) Control the input of chlorine to avoid excessive input

(c) Separate out TCPA predominantly by cooling the post-reaction solvent to around 40 degrees Celsius for crystallization in order to take advantage of the difference in the solubility of TCPA and HCB vis-à-vis the reaction solvent (chlorosulfonic acid) by temperature (furthermore, cool the filtrate to 0-25 degrees Celsius to separate out HCB, which is to be recycled as the reaction solvent).

According to the information in the patent application, the reaction control in (a) and (b) makes it possible to reduce the concentration of HCB "to around several hundreds ppm normally, i.e. to 300ppm or less under suitable conditions, and to 200ppm or less under more suitable conditions" and ensure HCB content of 200ppm or less when (c) is included (around 115ppm based on the results of experiments shown in the published information about the patent application).

However, since each method entails a decline in both the productivity and purity of TCPA, the reduction in the output of by-product HCB would lower the yield of TCPA production and push up production costs.

This company introduced the following control method in 1996 to reduce by-product HCB (but without the crystallization of the reaction solvent in (c):

(a) Strengthen the temperature control to 120 degrees Celsius plus or minus 5 degrees Celsius as against the prescribed reaction temperature of 120 degrees Celsius plus or minus 10 degrees Celsius

(b) End the reaction after the analysis of TCPA around 99.0% as against the prescribed end to the reaction at the TCPA production of 99.0% or over, whereas previously, the reaction was brought to an end after the TCPA analysis closed to 99.9%.

Due to the above-described control method, the amount of by-product HCB declined substantially from some 1,200ppm-2,100ppm (n=9) prior to 1996 to some 500ppm-900ppm (n=17) between June 1996 and December 1997.[4]

6. HCB Reduction Measures after TCPA Manufacturing Process

(1) Recrystallization Refinement by Solvent

Some companies deal in TCPA with HCB concentrations of 500ppm or less as merchandise (high-purity product grade), using recrystallization refinement.

Specifically, recrystallization refinement can produce TCPA with a low HCB concentration by controlling the cooling temperature and the number of recrystallizations after an organic solvent and crude TCPA are mixed at a certain rate of weight, heated and dissolved.

One company is not yet producing TCPA with a HCB concentration of 500ppm or less on a commercial basis, but had produced it in a pilot project. Another company also undertakes recrystallization refinement of TCPA using a solvent and actually had a record of made-to-order production of TCPA with HCB concentrations of 100ppm or less (see the table below). Thus, while the current state of responses varies from company to company, it seems that this method is being recognized as effective in reducing the HCB content.

TCPA by Two Manufacturers (Grading by HCB Concentration)

(a) Case of Company A

HCB concentration grade	below1000ppm	500ppm or less	50ppm or less	2-5ppm
Status of production (product)	In mass-production	No production on a commercial basis	Pilot production conducted	Experiment at a pilot plant
Refinement method	No refinement	Recrystallization	Recrystallization + α (some form of refinement)	Not known (refinement method different from recrystallization to the left)

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[4] An analysis by the same company.

Analytical value of samples with HCB concentration of 50ppm or less	・Pilot products: 3.6ppm, 3.3ppm, 6.2ppm ・Laboratory product 1: 42.9ppm ・Laboratory product 2: 37.1ppm

(b) Case of Company B

HCB concentration grade	1000ppm or less	100ppm or less	50ppm or less	5ppm or less?
Status of production (product)	In mass-production	Record of made-to-order production	Record of small-amount production	Unknown
Refinement method	No refinement	Repeat recrystallization twice	Repeat recrystallization three times	Unknown
	・ Possible to reduce HCB by 80% in single recrystallization; HCB can be reduced to some 200ppm in first recrystallization, to some 80ppm in second recrystallization, and to some 40ppm in third recrystallization			
Analytical value of samples with HCB concentration of 100ppm or less	・Made-to-order products: 70ppm, 160ppm, 69ppm			

Source: Prepared by the Committee Secretariat based on hearings with companies.

(2) Recrystallization Refinement Experiment Using Solvent in (1)

On the basis of the information obtained by the Committee, Chemicals Evaluation and Research Institute, Japan (CERI) conducted an experiment on the recrystallization refinement of TCPA using the solvent as described in (1) above. The conditions and results of the experiment are shown below:

- HCB concentration of TCPA used in experiment: 461ppm and 960ppm
- The solvent was added to 50g of TCPA, which was dissolved through heating, and then cooled for recrystallization. The crystallization was filtrated, cleansed and dried for weight measurement and analysis.
- The above-mentioned recrystallization refinement was repeated three times.

(a) TCPA Yield and HCB Reduction Rate (n=3 average) by Recrystallization using Sample with HCB Concentration of 461ppm

No. of refinement	1st	2nd		3rd	
Yield of TCPA	69.9%	2nd alone	85.0%	3rd alone	82.6%
		1st + 2nd	59.4%	1st + 2nd + 3rd	49.1%
Reduction rate of HCB (HCB concentration)	63.7% (167ppm)	2nd alone	60.9% (65ppm)	3rd alone	67.9% (21ppm)
		1st + 2nd	85.5% (65ppm)	1st + 2nd + 3rd	95.4% (21ppm)

(b) TCPA Yield and HCB Reduction Rate (n=3 average) by Recrystallization using Sample with HCB Concentration of 960ppm

No. of refinement	1st	2nd		3rd	
Yield of TCPA	80.0%	2nd alone	87.0%	3rd alone	85.3%
		1st + 2nd	69.6%	1st + 2nd + 3rd	59.3%
Reduction rate of HCB (HCB concentration)	65.5% (331ppm)	2nd alone	66.5% (110ppm)	3rd alone	64.3% (39ppm)
		1st + 2nd	88.6% (110ppm)	1st + 2nd + 3rd	95.9% (39ppm)

The above results supported the fact that the HCB concentration in TCPA can be reduced through recrystallization by the solvent.

The single recrystallization refinement produced a TCPA yield of around 70-80% and a HCB reduction rate of around 65% (or the reduction by around two-thirds). Furthermore, the repetition of recrystallization refinement three times can reduce the

HCB concentration by up to 95%, but the TCPA yield in this case declined to around 50-60%. In addition, it was confirmed that the single recrystallization refinement of the sample (with the recalibrated HCB concentration of 426ppm) in (a) above, when a solvent with a weight ratio to TCPA half of the above example was added and the rest of the same procedure as above was applied, significantly improved the TCPA yield to 80.6% while the HCB reduction rate was somewhat lower at 57.4%.

(3) Recrystallization Using Other Solvents

Some other companies also conducted recrystallization experiments using solvents other than those used in the above-mentioned experiment. The results of these experiments are as follows:

(a) An example of experiment on a beaker scale:

- HCB concentration of TCPA used in the experiment: 1,074ppm.
- Solvents were added to 20g or 10g of TCPA, which was then heated, and after the visual confirmation of dissolution, was cooled and crystallized. Then, the crystallization was filtrated, cleansed and dried for weight measurement and analysis.

Recrystallization solvent	A	B	C	D
TCPA yield	① TCPA 20g solvent 87% for 100ml ② TCPA 20g solvent 91% for 50ml	① TCPA 10g solvent 73% for 60ml ② TCPA 20g solvent 68% for 120ml	TCPA 10g solvent 93% for 170ml	TCPA 10g solvent 81% for 50ml
HCB reduction rate (HCB concentration)	① 85% （161ppm） ② 84% （168ppm）	① 81% （207ppm） ② 83% （176ppm）	85% （156ppm）	37% （674ppm）

Source: Prepared by the Committee Secretariat based on hearings with companies.

(b) An example of experiment on a test tube scale

- HCB concentration of TCPA used in the experiment: 886ppm
- 2g of TCPA and 18g of a solvent were put into a covered test tube, which was

then heated, and after the visual confirmation of dissolution, was cooled and crystallized. Then, the crystallization was filtrated, cleansed and dried for weight measurement and analysis.

Recrystallization solvent	E	F	G	H
TCPA yield	67.5%	34%	66.5%	35.0%
HCB reduction rate (HCB concentration)	96.5% （31ppm）	95.1% （43ppm）	95.0% （44ppm）	98.0% （18ppm）

Source: Prepared by the Committee Secretariat based on hearings with companies.

7. The BAT Level for TCPA

(1) The Base of Establishing the BAT Level

One company knew from around 1995 that HCB was generated as a by-product in the manufacturing process of TCPA, and this company reduced the concentration of by-product HCB to some 500ppm-900ppm about 10 years ago by controlling the reaction temperature.

However, the contamination level of the by-product HCB gradually increased due to antiquated equipment, and constantly exceeded 1,000ppm in around 2003.

At present, when TCPA products of two major manufacturers are compared, the product of one company has average HCB concentrations in excess of 2,000ppm but its selling price is higher than the product of another company with a lower HCB concentration. In this regard, it is difficult to believe that the HCB contamination level of some 2,000ppm is the BAT level economically.

Next, on the basis of Sections 5 and 6 above, technological elements to be considered in the establishment of the BAT level concerning the HCB concentration in TCPA include (1) reaction control, including the reaction temperature; (b) control of the temperature of TCPA crystallization in the post-reaction solvent; and (c) crystallization refinement of TCPA obtained in the reaction.

(a) Reaction Control

The publicized information about the patent application mentioned in (5) above indicates that the HCB concentration can be reduced to several hundreds ppm by controlling the reaction temperature and the extent of chlorination. Given it was possible to reduce the HCB concentration to about 500-900ppm 10 years ago and also considering the level of technology at present, it seems fully feasible to hold down the HCB concentration to similar levels with sufficient temperature control etc. in the manufacturing process.

Another company that manufactures and sells a high grade product with a lower HCB concentration (the standardized concentration of less than 1,000ppm) uses a manufacturing method that “changes conditions of synthesis (instead of recrystallization refinement).”

(b) Crystallization from the Post-Reaction Solvent

The same publicized information about the patent application as (1) above indicates that it is possible to separate out TCPA dominantly and reduce the HCB content in final TCPA to 200ppm or less (around 115ppm in the experiment) by cooling the post-reaction solvent to around 40 degrees Celsius for crystallization in order to take advantage of the difference in the solubility of TCPA and HCB vis-à-vis the reaction solvent (chlorosulfonic acid) by temperature.

In practice, however, the patent applicant did not adopt this method, and instead used the method of reaction control in (a). As for the manufacturing process of another company, details for which are not necessarily clear, the control of the temperature for TCPA crystallization from the post-reaction solvent is not so difficult technologically, and it seems to be a measure that can be introduced without too much of a cost burden.

(c) Recrystallization Refinement of TCPA

Regarding refinement after the manufacturing process, there have already been cases of shipments of high grade products with low HCB concentration (high-purity TCPA) by multiple companies adopting recrystallization refinement with the solvent in Section 6 (1) above.

While details about the refinement method are not known, the HCB concentration in the “high-purity TCPA” samples is less than 10ppm and around 100ppm.

Furthermore, one company reported that refinement using this solvent can reduce HCB concentration by 80% with a single recrystallization, with HCB concentration reduced to some 200ppm in the first recrystallization, to some 80ppm in the second and to some 40ppm in the third.

The recrystallization refinement experiments conducted by the Chemicals Evaluation and Research Institute, Japan (CERI), have confirmed that a single recrystallization refinement can reduce HCB by around 65% (with a TCPA yield of 70-80%) and that three repeated recrystallization refinements can reduce HCB by around 95% (with a TCPA yield of 50-60%). These experiment results somewhat differ from the information collected through the hearings in some aspects, but such differences can be considered to reflect the differences in the conditions of recrystallization processes, which have not been accurately understood, as well as differences in the scales of the experiments. Despite this, however, even under conditions in these experiments that were not necessarily optimized, it was confirmed that the recrystallization refinement method can at least reduce HCB content by 65% with a TCPA yield of 70-80%.

On the basis of present price differentials among TCPA products of respective grades, recrystallization refinement is likely to push up costs by some 25-40% for a single refinement process.

Incidentally, planned selling prices for high grade TCPA with a HCB concentration of some 50ppm or less are higher than those levels. For these products, one company claims that it goes through three recrystallization processes, while another company says it uses a single recrystallization plus α (meaning an undisclosed refinement process).

Meanwhile, recrystallization refinement using other solvents can be expected to reduce HCB levels. For example, in beaker-scale experiments, Solvent A achieved a TCPA yield of about 89% and a HCB reduction rate of around 85%, while Solvent B realized a TCPA yield of about 71% and a HCB reduction rate of around 82% (see Section 6. (3)(a) above). However, the use of these solvents in large quantities is deemed not desirable in terms of fire prevention as well as from the occupational health and safety standpoint.

(2) The BAT Level for TCPA

Given the above results, the approach to the BAT level significantly differs depending on whether recrystallization refinement is adopted or not.

The adoption of recrystallization refinement naturally pushes up costs, including those for solvents, treatment and personnel. However, if a single recrystallization using the solvent in Section 6 (1) above can reduce HCB concentration by 65-80%, despite a rise of around 25-40% in the price of TCPA, it seems important from the standpoint of preventing environmental contamination to carry out recrystallization refinement at least once.

More specifically, it is possible to reduce HCB content to several hundreds ppm (one company actually reduced it to 500-900ppm) by controlling temperatures in the manufacturing process, and a further reduction by the subsequent adoption of recrystallization refinement is considered to make it possible to further lower HCB concentration to at least 200ppm or less.

Moreover, while the feasibility of adopting this procedure remains uncertain under current circumstances, the publicized information in the patent application (the application was rejected for reasons of easy conception) suggests that HCB concentration can be reduced to 200ppm or less by controlling the TCPA crystallization temperature to a certain level even without conducting the recrystallization refinement of TCPA.

In terms of the economic aspects, the relationship between the (planned) selling prices and the concentration of HCB for one company already making sample shipments of high-purity products indicates that prices of TCPA with a HCB concentration of less than 200ppm are showing sharp rises.

Under these circumstances, therefore, it seems appropriate to adopt “200ppm” as the BAT level.

The recrystallization refinement by the solvent in Section 6 (1) above, which is one basis to set the BAT level in this consideration, was based on information from several companies. While the sources of this information are limited to these companies, given that much of the TCPA currently in use in Japan is being manufactured by these companies, it is deemed appropriate to establish the BAT level by reference to this information. However, it is still necessary for the government to make concerted efforts to collect more information and substantiate and confirm what such information indicates.

In addition, the Committee has information that the manufacture of TCPA with a HCB concentration far lower than this BAT level (200ppm) is already under way and the actual supply is about to begin. At present, however, since there are many unknowns about whether such products can be supplied in a stable manner, or their technical details, it is difficult to consider the BAT level immediately on the basis of this information.

8. Positioning of the BAT Level and Future Treatment

As already pointed out earlier, it is necessary to reduce the generation as by-product of Class I specified chemical substances regulated under the CSCL as much as is technically and economically feasible. Therefore, after the implementation of the proposed BAT level, the manufacture, import or use of TCPA with HCB concentrations higher than the BAT level would not be permitted under CSCL.

It is deemed appropriate to set a certain get-acquainted period before the entry into force of the proposed BAT level (200ppm) in consideration of the time required for the start of the actual manufacture and recrystallization refinement as well as the fact that the entire amount of TCPA in use in Japan is being imported from overseas.

Therefore, it is necessary for the government to promptly publicize the proposed BAT level and the approach it has taken to its establishment in order to facilitate prompt responses by the companies affected.

Meanwhile, after the publication and entry into force of the proposed BAT level, TCPA makers are being called upon to exert consistent efforts to supply TCPA with as low as possible HCB concentration regardless of the proposed BAT level (200ppm), given the fact that some makers are already making sample shipments of TCPA with a HCB concentration (50ppm or less) far less than the proposed BAT level.

Thus, the proposed BAT level is nothing more than a criteria at the moment, and it should be noted that going forward the BAT level needs to be lowered through consistent and concerted efforts by TCPA makers. Considering this, TCPA makers need to recognize that they should constantly move toward further reduction of the HCB concentration in TCPA through new technological development and management efforts. In particular, regarding TCPA with a HCB concentration far lower than the proposed BAT level already under consideration by some companies, it should be noted that the feasibility of the stable supply of these products will be assessed going forward and that, depending on the results of this assessment, it can be assumed that the BAT level may be established on the basis of these products in the future. 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 periodically (for example, about six months after the implementation of the proposed BAT level) in order to reconsider and review the BAT level on the basis of newly obtained information.

Furthermore, TCPA users (dye and pigment makers, for example), with full recognition that HCB is a Class I specified chemical substance, are strongly expected to strive to procure and use TCPA with a HCB concentration less than the proposed BAT level.

9. Proper Measures regarding HCB Removed in the TCPA Manufacturing Process

Following the establishment of the BAT level, it is expected going forward that the small quantity of HCB unintentionally generated in the TCPA manufacturing process must reduced as much as technically and economically possible in terms of the HCB concentration of TCPA to be shipped and used. On the other hand, there remains a concern about the possibility of removed HCB contained in wastewater from TCPA makers being released into the environment.

In particular, if the recrystallization refinement for TCPA, currently considered the BAT level technology, is applied, the elevated concentration of HCB may be contained in the solvent used for the refinement process. Furthermore, the post-reaction solvent (chlorosulfonic acid) also contains a considerable amount of HCB. Thus, it is essential for TCPA makers to fully recognize these facts and appropriately manage and treat reaction solvents after the reaction is completed as well as solvents after the recrystallization refinement, and at the same time adopt strict treatment such as measures to prevent workers engaged in this process from being exposed to HCB.

It is also necessary for TCPA makers to conduct a periodical analysis of other wastewater in order to monitor the actual status of HCB releases, and as necessary, carry out proper wastewater treatment to avoid the release of HCB into the environment as part of measures to prevent the environmental contamination by HCB.

10. Analytical Methods for HCB Contained in TCPA

For the quantitative analysis of HCB contained in TCPA, it is considered that a method should be adopted that can measure in a stable manner the concentration of one-tenth (20ppm) of the BAT level (200ppm) as the quantitation limit.

As an analytical method for this purpose, as listed below, an easy and appropriate method to determine a quantity of HCB by using a gas chromatograph/electron capture detector (GC/ECD) or gas chromatograph/mass spectrometer (GC/MS) after taking a precise amount of a sample is to dissolve it into acetone and other solvents in constant volumes (See Annex 7). In order to ensure the accuracy of measurement methods, determination the recovery of HCB and method blanks should be examined beforehand to ascertain if there are any problems involved in measurement methods to be adopted. In the sampling, as much effort as possible should be exerted to ensure that the samples are appropriate and representative.

(1) Sample Preparation Procedures

Take a precise amount of a sample, dissolve it into a solvent (acetone, etc.) in which TCPA is soluble, and then mix it thoroughly. Transfer the sample solution to a volumetric flask and obtain a constant volume by filling the volumetric flask with the solvent up to the marked line to use it as a measuring sample. Visually confirm that the TCPA crystallization is completely dissolved. Purify the sample solution as necessary for a measuring sample. Since the HCB recovery may deteriorate in conducting purification or concentration, it is necessary to consider beforehand sample preparation procedures that can ensure a sufficient level of HCB recovery. Since HCB is volatile, extra care is necessary for concentration procedures. When a sample solution is dried at the time of concentration by nitrogen gas flow or other methods, the HCB recovery rate is confirmed to decline substantially. Also, it is necessary to confirm through method blanks that reagents to be used for analysis do not pose any problems for the measurement. Because HCB is highly toxic, inhalation, accidental ingestion or direct dermal contact with it must be avoided as much as possible. The pretreatment room and laboratory shall be well-ventilated, and the management of waste water and wastes shall be sufficiently carried out. Furthermore, inhalation and accidental ingestion of other reagents, solvents etc. may be detrimental to the health of measurement staff and for this reason, the utmost care shall be taken when handling such substances, and the laboratory shall be sufficiently ventilated.

(2) Measurement Procedures

(a) Set up of measurement conditions

Set conditions for equipment used to ensure that the peak of HCB can be separated in a good condition from other chemical compounds on the chromatogram and that it responds in a stable manner. In particular, extra care is needed as the sample for measurement, when not refined, contains a large quantity of TCPA relative to HCB. In this case, it is necessary to confirm that HCB analysis is not interfered by TCPA or other impurities (such as tetrachlorobenzene) by GC/MS in total ion monitoring mode. If affected, analytical conditions (analytical columns, temperature-rising conditions, etc.) will need to be altered. Pretreatment clean-up (including silica gel cartridges) is also effective.

When the sample for measurement is purified, a method is adopted in advance that allows a sufficient recovery of HCB.

(b) Preparation of the calibration curve

Inject a certain quantity of the standard HCB solution prepared for calibration curve into the GC, and create the calibration curve from the relationship of the HCB peak area and concentration obtained. As for the standard solution concentration in this case, it is necessary that the concentration of the sample calculated on the basis of the quantity of the TCPA sample and the solvent dilution quantity include the BAT level and that the linearity of the calibration curve with the use of the standard solution with three or more concentration levels is secured.

(c) Quantitation limit

The quantitation limit is estimated by using the standard solution for preparing the calibration curve with the lowest HCB concentration that is sufficiently lower than one-tenth the BAT level. In other words, the standard solution for preparing the analytical curve with the lowest HCB concentration is analyzed repeatedly at least five times, and then the standard deviation is calculated on the basis of the 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 need 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, the quantitative determination of HCB can be made.

Part III The BAT Level for Solvent Red 135

1. Description of Solvent Red 135

The name, structural formula and physicochemical property of Solvent Red 135 are described in Annex 8. Domestic shipments (manufacture and imports) of Solvent Red 135 amounted to some 60 tons in FY2005. [5]

Solvent Red 135, by itself or in a mixture with other pigments, is being used for coloring resins such as acrylic, polycarbonate and polystyrene. These colored resins are mainly used for automotive parts and components (e.g. tail lamp covers, parts used for interiors), and the exterior of electrical equipment (e.g. office automation equipment and electrical home appliances).

In general, it is difficult to immediately replace Solvent Red 135 with other substances for dyes and pigments due to differences of their natures of coloring and durability. For automobile tail lamps in particular, it is said that because of weather resistance and other reasons, there is currently no resin that satisfies product specifications other than that colored by Solvent Red 135. For these uses, it is deemed difficult, at least under current circumstances, to move immediately toward to replacement by other substances by restricting the supply of Solvent Red 135.

2. HCB Contamination Level

Regarding the content of residual by-product HCB in Solvent Red 135, in addition to the data taken by manufacturers and importers, the government has conducted an analysis of HCB concentration in Solvent Red 135 samples provided by them after this particular case was revealed (see Annex 9).

As Annex 9 shows, as in the case of TCPA, there are cases where the HCB contamination level of the same lot varied depending on who conducted the analyses. Thus, it seems appropriate to present a certain unified method of analysis to confirm this in establishing the BAT level (see Section 10 to be described later).

3. Manufacturing Method of Solvent Red 135

The Solvent Red 135 manufacturing method is as follows. Solvent Red comes from reaction of TCPA with 1,8-diaminonaphthalene in the heated reaction solvent (the reaction formula is shown below). A final product is obtained following

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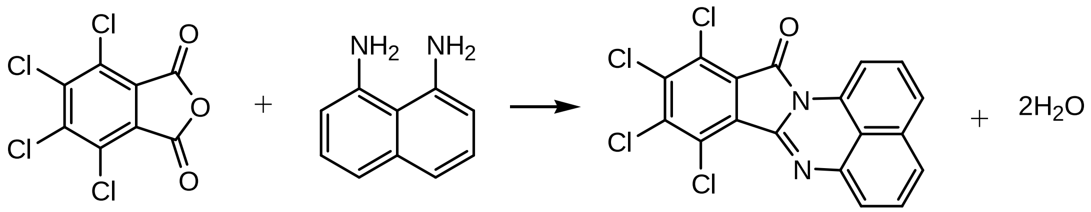
[5] The amount is the sum of shipments by six companies that reported their production or imports at the hearings.

cleansing and drying processes after separating Solvent Red 135 by cooling down the reaction liquid after the reaction. Kinds of reaction solvents used, reaction conditions (temperatures and reaction time), and post-reaction cleansing methods vary depending on manufacturers.



4. Residual HCB Concentration by Manufacturers

Since no chlorination process is involved in the manufacturing process for Solvent Red 135 and the reaction formula above does not assume any new generation of HCB as a by-product, it is considered that part of the HCB contained in material TCPA remains as a residual in the reaction product, Solvent Red 135.

Analysis results of the HCB concentration in Solvent Red 135 conducted by the government show that the residual HCB content in Solvent Red 135 varies by manufacturer, ranging widely from 0.084ppm to 310ppm (see the table below).

HCB Content in Solvent Red 135 by Manufacturer

Manufacturer	HCB Content
Company A	10～21ppm （n＝15） Average 16ppm
Company B	0.084～2.1ppm （n＝5） Average 0.74ppm
Company C	5.3～61ppm （n＝6） Average 29ppm
Company D	4.8～7.5ppm （n＝4） Average 6.3ppm
Company E	4.5～10ppm （n＝2） Average 7.3ppm
Company G	160～310ppm （n＝3） Average 220ppm

Source: Analysis results conducted by the Japanese government

5. HCB Reduction Measures in Solvent Red 135 Manufacturing Processes

(1) Manufacturing Methods and HCB Content

Manufacturers use different reaction solvents, which are broadly categorized into water-type solvents and organic ones. Companies A to E in the table above use organic solvents, while Company F uses water-type solvents to obtain the reaction.

In order to confirm changes in the content HCB in each stage of the manufacturing process, the government conducted an analysis of samples provided by one of the manufacturers that were taken mid-course in the actual manufacturing process. Specifically, the analysis targeted HCB concentration in the three sets of samples taken from the four stages; respectively, (a) from material TCPA, (b) after the reaction was completed (the sample immediately after filtration), (c) mid-course in the cleansing process, and (d) from the final product. The analysis results are as shown in the below table.

HCB Concentration at Each Stage of Solvent Red 135 Manufacturing Process

	HCB Concentration (ppm)		
(a) Material TCPA	1100	600	1400
(b) After reaction/ filtration	20	12	25
(c) After cleansing	17	10	22
(d) Final product	17	10	21

Source: Analysis results conducted by the Japanese government

An examination of the HCB-related material balance by one of the companies through a beaker-scale reenactment of the manufacturing process has confirmed that some 96% of the HCB content initially contained in the reaction liquid was separated and removed by the first cleansing with the use of a solvent, and a further 2.6% or so of the HCB content was separated and removed in another cleansing by a different solvent but two subsequent cleansings using other solvents removed little more HCB, leaving 1.3% of the original HCB content in Solvent Red 135.

Further, another company reported that it was able to substantially reduce the HCB content in the product by replacing a reaction solvent used in the past by another solvent with a low polarity.

As mentioned earlier, residual HCB concentration in Solvent Red 135 shows a tendency of varying depending on manufacturers, and this is considered to be related to the types of solvents they use in their manufacturing processes. In particular, the polarity of solvents is thought to significantly contribute to the allocation of HCB. When solvents have no polarity, the decline in the degree of supersaturation delays the rate of crystallization and thus the crystallization (Solvent Red 135) is expected to take in a lesser quantity of HCB. Furthermore, this is thought to raise the solubility of highly-hydrophobic HCB into solvents, thereby raising the distribution of HCB to solvents. In other words, a considerable proportion of HCB contained in material TCPA is distributed to reaction solvents and removed from the crystallization (Solvent Red 135) in the filtration process following the crystallization. On the other hand, Solvent Red 135 produced by the company using a water-type solvent has a higher HCB content, by one order or more, than that for other companies. It can be explained that a higher concentration of residual HCB is left in Solvent Red 135 not only because the very high degree of supersaturation makes it easy for a large quantity of HCB to be taken into products, but also because highly-hydrophobic HCB is not soluble in water-type solvents.

As for organic solvents, the analysis found that the content of HCB increases in proportion with the strength of the polarity of the reaction solvents. It can be construed that the use of a low-polarity solvent as the reaction solvent keeps the intake of HCB by Solvent Red 135 low to cause a greater content of HCB to transfer to the reaction solvent, thereby reducing the HCB concentration of Solvent Red 135.

(2) HCB Reduction Measures in Manufacturing Processes

Following the revelation of this case, one Solvent Red 135 maker has tried to improve its cleansing process as a measure to reduce residual HCB concentration. However, as shown in the table above, the analytical results point to only small changes in the content of HCB between the stage after the reaction/filtration and the post-cleansing stage, an indication of no reduction effect by cleansing.

This company further tested an additional cleansing process using the same kind of solvent as used in the reaction, but it only produced an impact that almost matched the effect of the earlier-mentioned additional cleansing. Another company also conducted a (beaker-scale) experiment to examine the effect of cleansing by several kinds of solvents. The result showed that, even when a low-polarity solvent considered to produce a greater reduction effect was used, the reduction effect was not so impressive, with a removal rate of only around 18% (the HCB content was reduced from 330ppm to 270ppm). Thus, considering cost effectiveness, additional cleansing methods mentioned in this section are judged to be not so practical.

As described above, the cleansing of Solvent Red 135 in the post-manufacturing stage does not significantly reduce HCB concentration. It is inferred that post-reaction cleansing only removes HCB on the surface of Solvent Red 135 and that it is difficult by this process to reduce the HCB taken into the crystallization.

6. Relationship between HCB Concentration in Material TCPA and Solvent Red 135

Figure 1 shows the relationship between the HCB concentration in material TCPA and that in Solvent Red 135 surely obtained from the material. Figure 2 shows the relationship between the HCB concentration in the material and the residual ratio (the percentage ratio of the HCB concentration in material TCPA and that in Solvent Red 135). In these figures, different plots correspond to each manufacturer that provided the samples. The figures use the analysis data conducted by the government wherever they are available, and in case of the absence of the government's analysis, they are substituted with results provided by companies concerned.

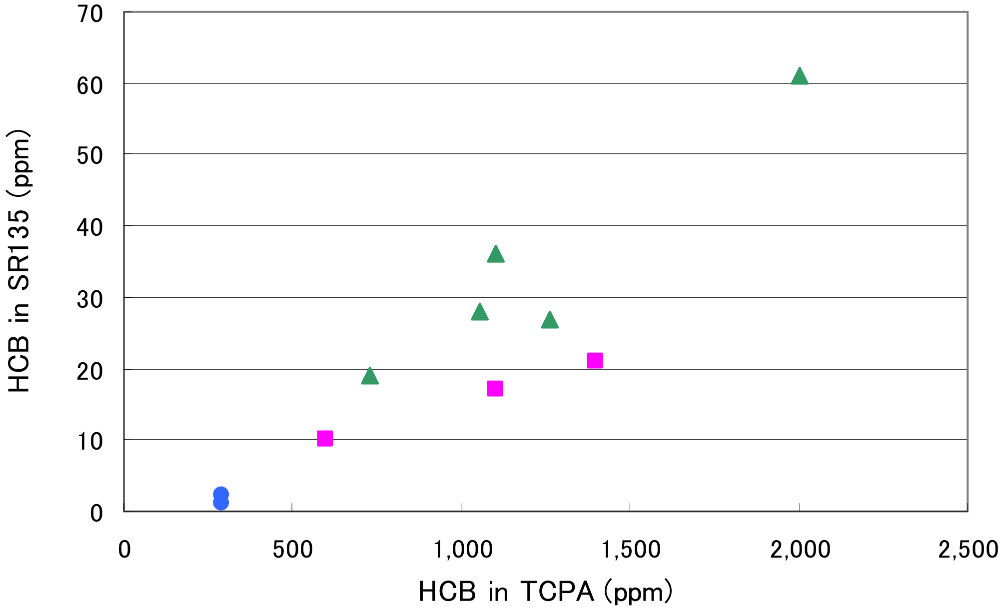


Figure 1. Relationship between the HCB concentration in Material TCPA and Solvent Red 135

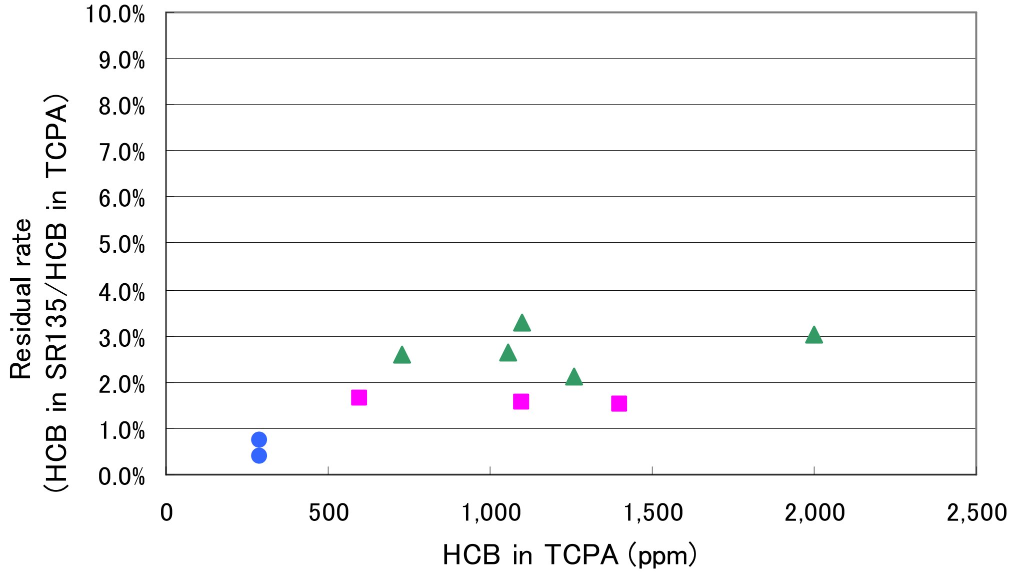


Figure 2. HCB Concentration in TCPA and the HCB residual rate

Figure 1 indicates that for each company, as the HCB concentration in the material (TCPA) increases, the HCB concentration in the product (Solvent Red 135) tends to increase.

Figure 2 also indicates that while the HCB residual rate varies among manufacturers, the differences are contained in a range of several percentage points (3.3% at the maximum). Meanwhile, though there are no detailed data, multiple companies reported at the Committee’s hearings that there is a corresponding relationship between the HCB content in materials and in products, and that roughly one-fiftieth to one-fortieth (2% to 2.5%) of the HCB concentration in material TCPA remains in Solvent Red 135 appears as residual HCB.

In Figure 2, data for one company shows a tendency that the HCB residual rate rises slightly as the HCB concentration in TCPA declines, but data for other companies do not back up this relationship and rather indicate that the residual rate stays within a certain range (2% to 3%) regardless of the HCB concentration in TCPA.

It is probable that the HCB residual rate is determined by the manufacturing process and the residual rate can be expected to vary significantly according to differences in processes. But the analytical results of companies that use organic solvents indicate that HCB residual rates, while showing minor differences, stayed within a range of several percentage points. Given that the residual rate is almost constant, it is assumed that, as shown in Figure 1, the HCB concentration in TCPA almost determines the quantity of the residual HCB in Solvent Red 135.

7. The BAT Level for HCB in Solvent Red 135

It is considered that the HCB contained in Solvent Red 135 is not a by-product in its manufacturing process but a residual of the part of the HCB already contained in material TCPA. Further, as summarized in Section 6 above, the existence of a clear corresponding relationship is suggested between the HCB content in material TCPA and that in Solvent Red 135. Therefore, it can be construed that the most important and effective measure to reduce HCB contained in Solvent Red 135 is to reduce HCB contained originally in material TCPA.

Meanwhile, the Solvent Red 135 manufacturing methods using organic reaction solvents already adopted by many manufacturers extract a considerable quantity of HCB into reaction solvents (or cleansing solvents) and thereby produce Solvent Red 135 with a very small content of HCB relative to the HCB concentration of material TCPA. It can be considered that these manufacturing processes themselves represent an effective measure in terms of the reduction of HCB contained in Solvent Red 135.

Some manufacturers are trying to reduce the HCB content by improving post-reaction cleansing processes. However, as it is deemed not easy to remove HCB taken in crystallized Solvent Red 135, it is hard to regard such post-reaction processes as appropriate, and it is also difficult to regard them as appropriate from the viewpoint of cost-benefit performance considerations.

Considering the above, a significant reduction of the HCB concentration in Solvent Red 135 from the current level is expected by the achievement of the BAT level for material TCPA discussed in Part II, rather than by further refinement of the manufacturing processes. For domestic manufacturers in particular, as there will be no more supply of TCPA with the HCB content higher than the BAT level after the implementation of the BAT level, it becomes possible to manufacture Solvent Red 135 with a HCB content that is certainly lower than the current levels.

As described in Section 6, the HCB residual rate in the manufacturing of Solvent Red 135 is limited to several percentage points (3.3% at the maximum) when organic reaction solvents are used. Considering this and the BAT level for TCPA (200ppm), it is assumed that the HCB content in Solvent Red 135 can be contained to the order of several ppm (at least less than 10ppm). Though there are no available data to show a range of HCB residual rates when Solvent Red 135 is actually manufactured using TCPA matching the BAT level (the HCB content of 200ppm or less), as far as Figure

2 indicates, it is hard to assume an extremely high residual rate (a rate in excess of 5%, for instance). On the basis of these considerations, it is deemed appropriate to set the BAT level for Solvent Red 135 at “10ppm” for the time being and apply this level in conjunction with the BAT level for TCPA.

Moreover, it is expected to be possible to manufacture Solvent Red 135 with a low HCB concentration of less than 1 ppm by adopting a manufacturing process that uses a reaction solvent with a polarity as extremely low as HCB. However, the use of such solvents is not desirable from the viewpoint of occupational safety and fire prevention. It is difficult to promote the use of such solvents also in view of the current situation where Japan is making efforts to get rid of organic solvents used in industrial plants.

8. Positioning of the BAT Level and Future Treatment

As already pointed out earlier, it is necessary to reduce the generation as by-products of Class I specified chemical substances regulated under CSCS as much as is technically and economically feasible. Therefore, after the entry into force of the proposed BAT level, the import or use of Solvent Red 135 with HCB content higher than the established BAT level would not be permitted under CSCL.

Since it is considered that HCB is not produced as a by-product in the manufacturing process of Solvent Red 135 and HCB remains only as a residual of HCB contained in material TCPA, in light of the interpretation of the term “manufacture” in CSCL, the practice of manufacturing Solvent Red 135 does not represent the manufacture (generation as a by-product) of HCB. However, given the existence of Solvent Red 135 imported and put on the market and the fact that a variety of products are being manufactured using Solvent Red 135, it is still necessary to establish the BAT level for Solvent Red 135.

It is deemed appropriate to set a certain get-acquainted period before the application of the proposed BAT level for Solvent Red 135 (10ppm), similarly as the BAT level for TCPA. It is necessary for the government to promptly publicize the proposed BAT level and the approach it has taken to its establishment in order to facilitate prompt responses by the companies affected. Meanwhile, there may be a certain time lag between the start of the supply of TCPA that meets the BAT level and the start of manufacture and shipments of Solvent Red 135 using such TCPA.

Given that some TCPA manufacturers are already beginning to supply TCPA with HCB content far lower than the BAT level (200ppm), Solvent Red 135 manufacturers are being called upon to exert constant efforts to supply Solvent Red 135 with an as low as possible content of HCB by trying to procure material TCPA with a lower HCB content regardless of the proposed BAT level.

The proposed BAT level is nothing more than a criteria at the moment, and it should be noted that the BAT level needs to be lowered going forward through rigorous efforts on the part of Solvent Red 135 makers. Considering this, Solvent Red 135 makers need to recognize that they should constantly move toward a further reduction of the HCB concentration in Solvent Red 135 through new technological development and management efforts. In particular, as pointed out in Part II, considering that the BAT level for TCPA can be expected to be reviewed in accordance with progress in TCPA manufacturing technology, it is appropriate to consider the BAT level for Solvent Red 135 as well when the BAT level for TCPA is reviewed. Therefore, it would be appropriate for the government to continue to strive to collect related information even after the enforcement of the proposed BAT level and convene the Committee periodically (for example, about six months after the entry into force of the BAT level) in order to reconsider and review the BAT level on the basis of newly obtained information.

Furthermore, Solvent Red 135 users (resin makers, for example), with full recognition that HCB is a Class I Specified Chemical Substance, are strongly expected to strive to procure and use Solvent Red 135 with a HCB concentration less than the proposed BAT level.

9. Proper Treatment of HCB Removed in the Manufacturing Process of Solvent Red 135

Finally, it has become known that most of by-product HCB (over some 95%) contained in material TCPA is transferred to reaction solvents (post-reaction filtrates) in the manufacturing process of Solvent Red 135. Thus, it is essential for Solvent Red 135 manufacturers to fully recognize these facts and ensure the proper treatment of post-reaction filtrates and adopt strict treatment, including measures to prevent workers engaged in the manufacturing process from being exposed to HCB.

In cleansing and other processes for Solvent Red 135 crystallized after the reaction, a small quantity of HCB may be contained in cleansing wastewater, though the quantity is deemed small relative to that in reaction solvents. Therefore, it is also necessary for Solvent Red 135 manufacturers to conduct a periodical analysis of wastewater in order to monitor the actual status of HCB releases, and as necessary, carry out proper wastewater treatment to avoid the release of HCB into the environment as part of measures to prevent environmental contamination by HCB.

10. Analytical Techniques for HCB Contained in Solvent Red 135

For the quantitative analysis of HCB contained in Solvent Red 135, it is considered that a method should be adopted that can measure in a stable manner the concentration of one-tenth (1ppm) of the BAT level (10ppm) as the quantitation limit.

Solvent Red 135 is not soluble in many organic solvents, and as pigments do not dissolve and the HCB inside cannot be extracted by Soxhlet extraction with solvents such as toluene, it is possible to underestimate the HCB content, and that could lead to actual shipments of products with HCB content higher than the BAT level.

For this reason, for an analytical method, as listed below, a method to determine a quantity of HCB in extracted liquids by using a gas chromatograph/electron capture detector (GC/ECD) or gas chromatograph/mass spectrometer (GC/MS) after taking a precise amount of a sample, dissolving it into sulfuric acid to obtain constant volumes and extracting HCB contained in solvents such as hexane and toluene is considered to be appropriate (See Annex 10). In order to ensure the accuracy of measurement methods, determination the recovery of HCB and method blanks should be examined beforehand to ascertain if there are any problems involved in measurement methods to be adopted. Because HCB is highly toxic, inhalation, accidental ingestion or direct dermal contact with it shall be avoided as much as possible. The pretreatment room and laboratory shall be well-ventilated, and the management of waste water and other wastes shall be sufficiently carried out. Furthermore, inhalation and accidental ingestion of other reagents, solvents, etc., may be detrimental to the health of measurement staff. For these reasons, the utmost care shall be taken when handling them and the laboratory shall be sufficiently ventilated. In addition, when sampling, as much effort as possible should be exerted to ensure the samples are appropriately representative.

(1) Sample Preparation Procedures

Take a precise amount of a sample, dissolve it into sulfuric acid and then mix it thoroughly. Transfer the sample solution to a volumetric flask and obtain a constant volume by filling the volumetric flask with sulfuric acid to the marked line. Visually confirm that the Solvent Red 135 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 equipment used. Extract HCB in the sulfuric acid solution with a solvent such as hexane or toluene. Clean up the extract liquid as necessary as a measurement sample. Other cleanup procedures include sulfuric acid treatment and water washing, the use of silica gel cartridges, and/or a combination of these procedures. It should be noted that the absence of refinement could deteriorate the GC injection port and analytical columns. Since HCB recovery may deteriorate in the extraction and clean-up processes, it is necessary to consider beforehand appropriate sample preparation procedures that can ensure a sufficient level of HCB recovery. Since HCB is volatile, extra care is necessary for condensation procedures. When a sample solution is dried at the time of concentration by nitrogen gas flow or other methods, the HCB recovery rate is confirmed to decline substantially. If possible, it is recommended to adopt a method to correct the recovery by adding internal standard substances. Internal standard substances that can be analyzed under the same conditions as HCB should be adopted in the preparation procedures. 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, γ－HCH (lindane) and other substances can be used. In the GC/MS (SIM) analysis, $^{13}C_6$-HCB that is labeled with ^{13}C for all carbon atoms of HCB may be used as internal standard substance. Also, it is necessary to confirm through method blanks that reagents to be used for the analysis do not pose any problems to the measurement.

(2) Measurement Procedures

(a) Set up of measurement conditions

Set conditions for instruments used to ensure that the peak of HCB can be separated in a good condition from other chemical compounds on the chromatogram and that it responds in a stable manner. Care is necessary as chemical compounds other than HCB exist in the sample for measurement. It is necessary to confirm that HCB analysis is not interfered with by other impurities by conducting GC/MS in total ion monitoring mode. If affected, the further purification and/or changes in analytical conditions (analytical columns used, temperature-rising conditions, etc.) are needed. When $^{13}C_6$-HCB is used as a reference substance, extra care is needed in the setting of measurement quantities as HCB fragment ion interferes with low-resolution GC/MS analysis. While M+2 and M+4 ions are measured, a resolving power of over 10,000 is necessary to ensure the non-interference of HCB in the samples with reference substances. When low-resolution GC/MS is used, it is necessary to respond by measuring M+6 and M+8 irons or using reference substances other than $^{13}C_6$-HCB.

(b) Preparation of the calibration curves

Inject a certain quantity of the standard HCB solution prepared for a calibration curve, and create the calibration curve from the relationship of the HCB peak area and concentration obtained. As for the standard solution concentration in this case, it is necessary that the concentration of the sample calculated on the basis of the quantity of the Solvent Red 135 sample and the solvent dilution quantity include the BAT level and that the linearity of the calibration curve with the use of the standard solution with three or more concentration levels is secured. When a reference substance is used, a quantity is determined by the response factor (RF) or the calibration curve using an internal standard.

(c) Quantitation limit

The quantitation limit is estimated by using the standard solution for preparing the calibration curve with the lowest HCB concentration that is sufficiently lower than one-tenth the BAT level. In other words, 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 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 need 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, a quantitative determination of HCB can be made.

【Annex 1】

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.

<u>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.</u>

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 2】

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)		
(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 3】

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

1. Purpose

The Committee is designed to consider and evaluate the technically and economically best feasible levels for reduction (BAT reduction levels) of specified chemical substances under CSCL concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. that are generated as by-products in the process of synthesizing chemical substances.

2. Format

The Committee is established as the joint committee of three Ministries (Ministry of Health, Labour and Welfare, Ministry of Economy, Trade and Industry, and Ministry of the Environment), and composed of experts asked to join by the respective ministries from such areas as chemicals and materials, industrial processes, analysis, economics, the environment, statistics and quality control.

3. Procedures for Consideration

(1) Consideration on the basis of materials submitted by companies

The three Ministries instruct the companies concerned to submit necessary information when they deem it necessary to consider the technically and economically best feasible reduction levels for specified chemical substances contained as by-products in manufactured or imported chemical substances.

Companies that handle substances subject to the evaluation, in compliance with the requests from the three Ministries, submit information on such matters as names, manufacturing methods, constituents and contents of by-product specified chemical substances to the three Ministries as reference materials for the Committee.

(2) Hearings with companies

The Committee, in its consideration on the basis of materials described in (1), asks the companies concerned to attend its meetings to offer explanations as necessary.

(3) Consideration on the basis of results of investigations by the government

The three Ministries conduct investigations on the following matters as necessary and submit their results to the Committee:

- Uses of chemical substances that include specified chemical substances
- Concentration of by-product specified chemical substances in chemical substances

(4) Evaluation of BAT reduction levels

The Committee, on the basis of the above consideration, evaluates the technically and economically best feasible reduction levels.

When it is deemed necessary to make the above consideration in an efficient and focused manner within a short period of time, the Committee makes flexible responses, including the holding of Committee meetings, by narrowing the scope of participating Committee members to conduct hearings with the companies concerned.

4. Handling of Committee meetings and their results

- The Committee, in principle, meets behind the closed doors as it deliberates on matters that fall under the category of trade secrets. Committee members have a confidentiality obligation regarding trade secrets they learn through activities of the Committee.
- Materials submitted to Committee meetings as reference materials are not to be made public in principle. In particular, materials submitted by companies concerned that contain trade secrets are collected after Committee meetings. However, materials that have no particular reason to be classified, including the results of investigations conducted by the government, are to be publicized in principle.

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 4】

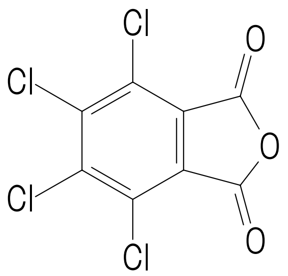
Committee Meetings

Date	Meeting	Agenda
April 4 (Friday)	1st meeting (1st plenary session)	・Establishment of the Assessment Committee on the BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product ・Generation of by-product hexachlorobenzene ・Procedures for consideration going forward
April 21 (Friday)	2nd meeting (1st WG session)	Hearing (TCPA manufacturers/importers)
May 12 (Friday)	3rd meeting (2nd WG session)	
May 26 (Friday)	4th meeting (3rd WG session)	
June 2 (Friday)	5th meeting (4th WG session)	Hearing (Solvent Red 135 manufacturers/importers)
June 9 (Friday)	6th meeting (5th WG session)	
June 16 (Friday)	7th meeting (6th WG session)	
June 30 (Friday)	8th meeting (7th WG session)	
July 3 (Monday)	9th meeting (8th WG session)	Hearing (Analytical organizations)
July 12 (Wednesday)	10th meeting (2nd plenary session)	Draft report on TCPA
July 20 (Thursday)	11th meeting (3rd plenary	Report on TCPA (draft revision), report on SR135 (draft)

	session)	
August 3 (Thursday)	12th meeting (4th plenary session)	Report (draft)
October 12 (Thursday)	13th meeting (5th plenary session)	Revision to the report based on public comments

【Annex 5】

Description of TCPA

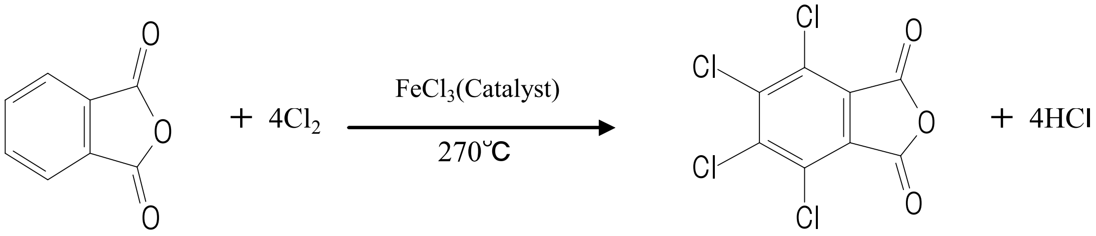
1	Structural formula			
		English name Phthalic anhydride,tetrachloro- CAS registration number: 117-08-8 RTECS number: TI3450000 ICSC number: 1374 EC number: 607-242-00-1		
2	Composition formula	$C_8Cl_4O_3$		
3	Molecular weight	285.90		
4	CSCL			
	Category	Existing chemicals		
	CSCL number	3-1423	CSCLnumber	3-62
	Name on CSCL existing chemicals list	Phthalic anhydride tetrachloride	Name on CSCL existing chemicals list	Mono (or -tetra) bromoacetic (or chloro) benzene, mono (or –di) carboxylic acid (or chloride and anhydrous)
5	Physicochemical property			
	Appearance	White powder（ICSC）		
	Density	$1.49 g/cm^3$		
	Melting point	255℃（ICSC）		
	Boiling point	371℃（ICSC）		
	Vapor pressure	1.29×10^{-7} mmHg (estimate value: 25℃) (SRC MPBPWIN)		
	Water solubility	0.4g/100mL（20℃）（ICSC）		
	LogPow	4.65 (estimate value) (SRC KOWWIN)		
6	Solubility in organic solvents(g/100g-Solvent)			
	acetone	3.1(25℃)、5.6（49℃） Beilstein		
	benzene	4.0(25℃)、11.9（76℃） Beilstein		
	chlorobenzene	2.7(25℃)、8.6（76℃） Beilstein		
	o-dichlorobenzene	4.0mg(25℃)、9.1mg（76℃） Beilstein		
	tetrachlorobenzene	0.15(24℃)、0.68（76℃） Beilstein		

Domestic shipments: about 107 tons (the average for 1996-2005)
about 30 tons (actual for 2005)）

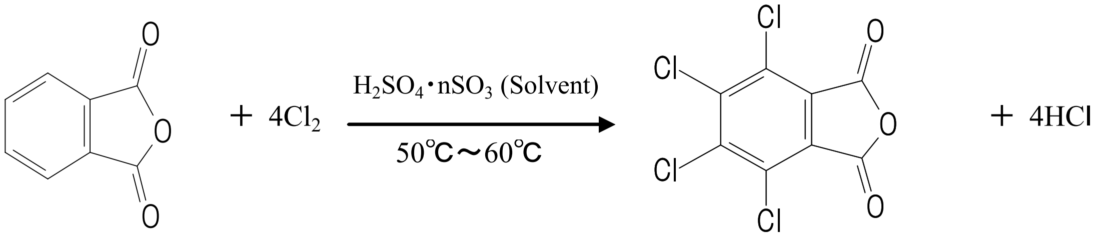
TCPA Manufacturing Method

1 Method to turn phthalic anhydride into the molten state by heating it to 270 degrees C and make it react with the introduction of chlorine gas with iron or ferric chloride as a catalyst without using any solvent (Gas phase method)

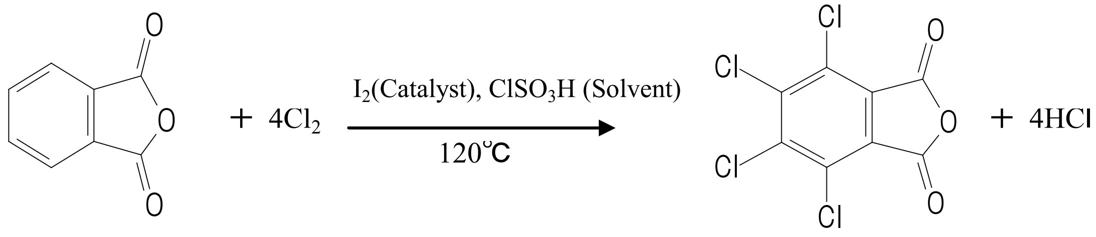
2 Method to cause a gas phase reaction between phthalic anhydride and chlorine gas with ferric chloride as a catalyst (Gas phase method)



3 Method to cause a solution phase reaction between phthalic anhydride and chlorine gas at 50 to 60 degrees C using fuming sulfuric acid as a solvent (Liquid phase method)
(Example)
Main raw material: phthalic anhydride, chlorine
Secondary raw material: fuming sulfuric acid

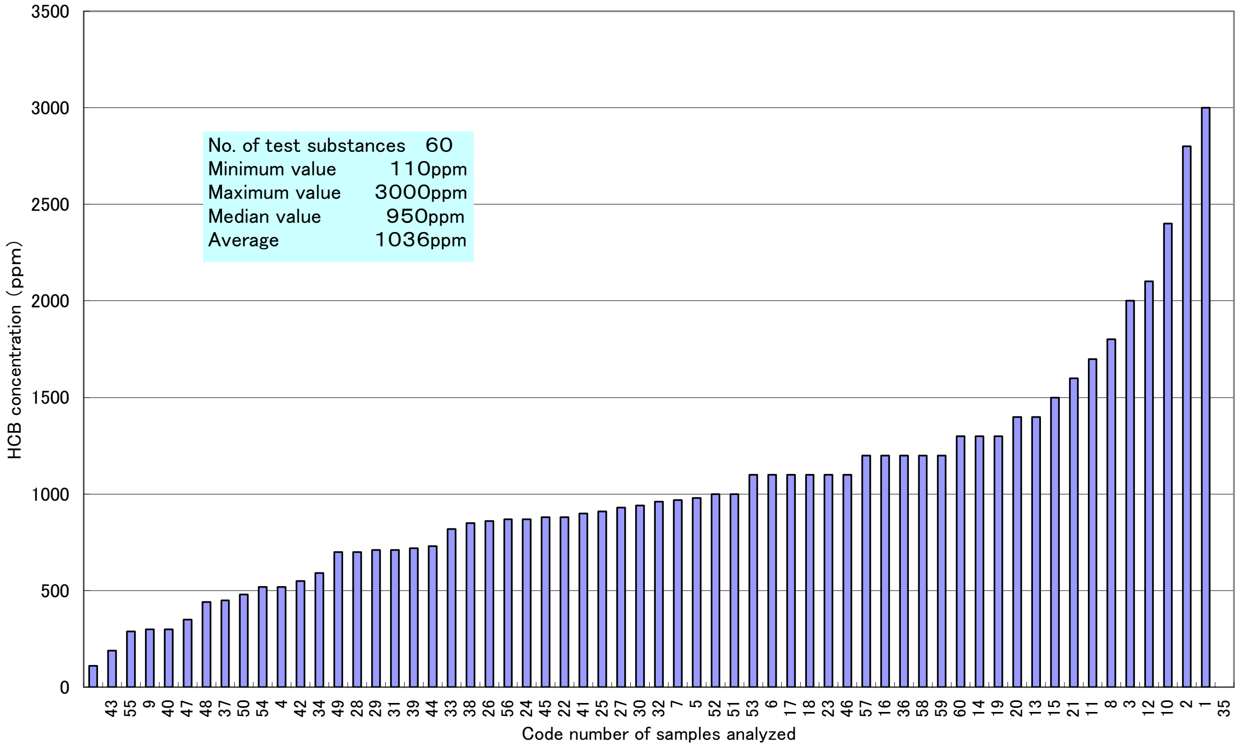


4 Method to cause a solution phase reaction between phthalic anhydride and chlorine gas using chlorine gas as a solvent and also using inactive chlorosulphonic acid as hydrochloric gas generated
(Liquid phase method)
(Example)
Main raw material: phthalic anhydride, chlorine
Secondary raw material: chlorosulphonic acid, iodine, etc.



【Annex 6】

HCB Concentration in TCPA Provided by Companies (Results of Analysis by the Government)



【Annex 7】

Example of Measurement of HCB Content in TCPA Using GC/MS

I. GC/MS measurement conditions

Column: DB-5 (internal diameter 0.32mm, length 30 m, film thickness 0.25 μm, made by J&W Scientific)

Oven temperature: 80 degrees Celsius (1 min.)→20 degrees Celsius/min→160 degrees Celsius→5degrees Celsius/min→200 degrees Celsius→40 degrees Celsius/min→280 degrees Celsius
Injection port temperature: 280 degrees Celsius
Transfer line temperature: 280 degrees Celsius
Ionization voltage: 70V (EI mode)
Ion detection method: Selected ion detection (SIM) method
SIM conditions: Monitor ion (underline for quantitative determination, others for qualitative determination) *m/z* 283.8, 285.8
Carrier gas: helium (constant flow mode at 1.5 mL/min)
Injection volume: 1μL (splitless)

II. Preparation method for sample solution

0.01 g of a sample put into a 100mL volumetric flask to prepare 100 mL of test solution with acetone.

III. Preparation of the calibration curve

The concentration of HCB standard solutions prepared with acetone ranged from 0.5 to 1000ng/mL gradually.

IV. Quantitative determination and confirmation

The quantitative determination was made by obtaining the HCB peak area through the GC/MS (SIM) measurement. Confirmation was made in the SIM measurement by comparing the relative intensity ratio of qualitative ion with standard solution.

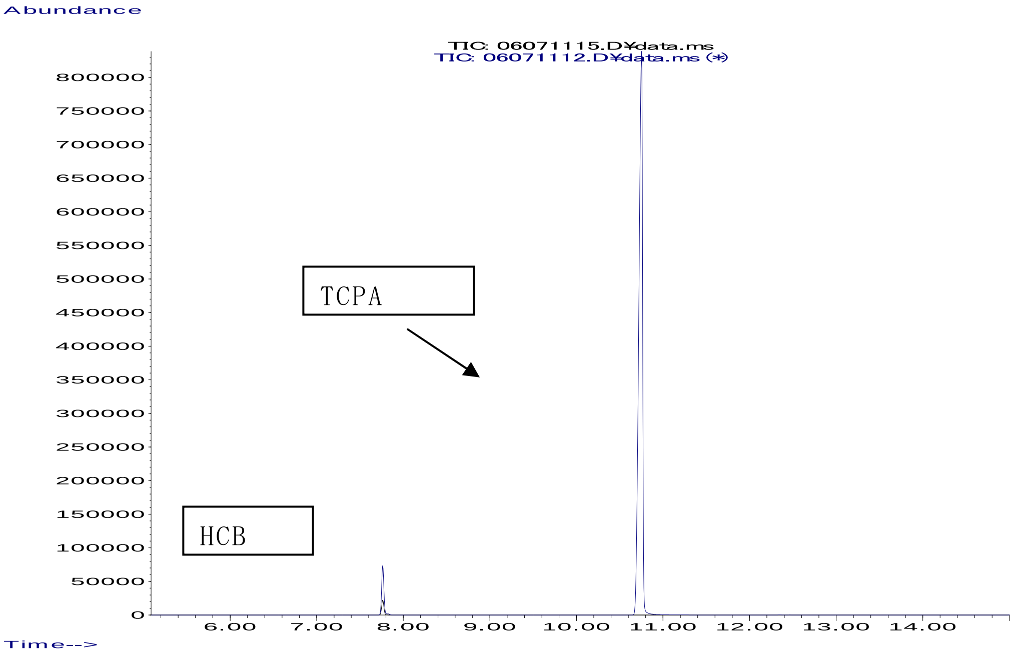


Figure 1 Chromatogram of TCPA Samples

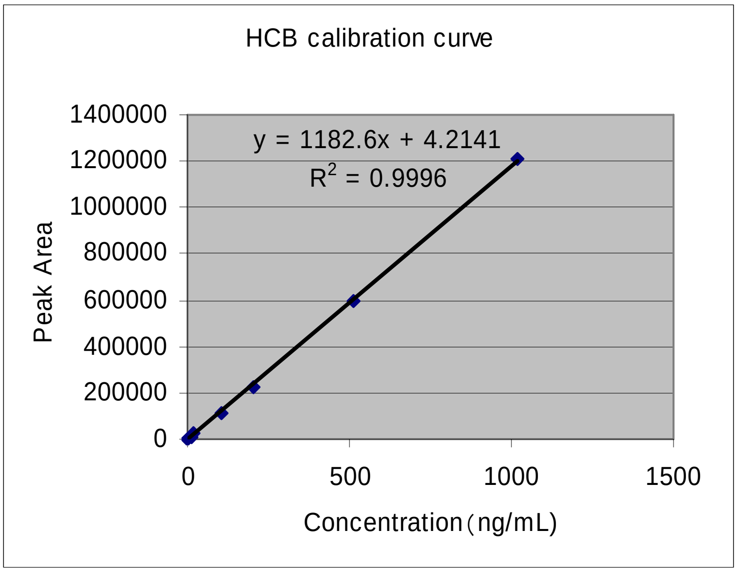
V. Results and Discussion

1. Consideration of analysis conditions

The separation of TCPA and HCB proceeded well. The chromatogram of TCPA prepared samples is shown in Figure 1.

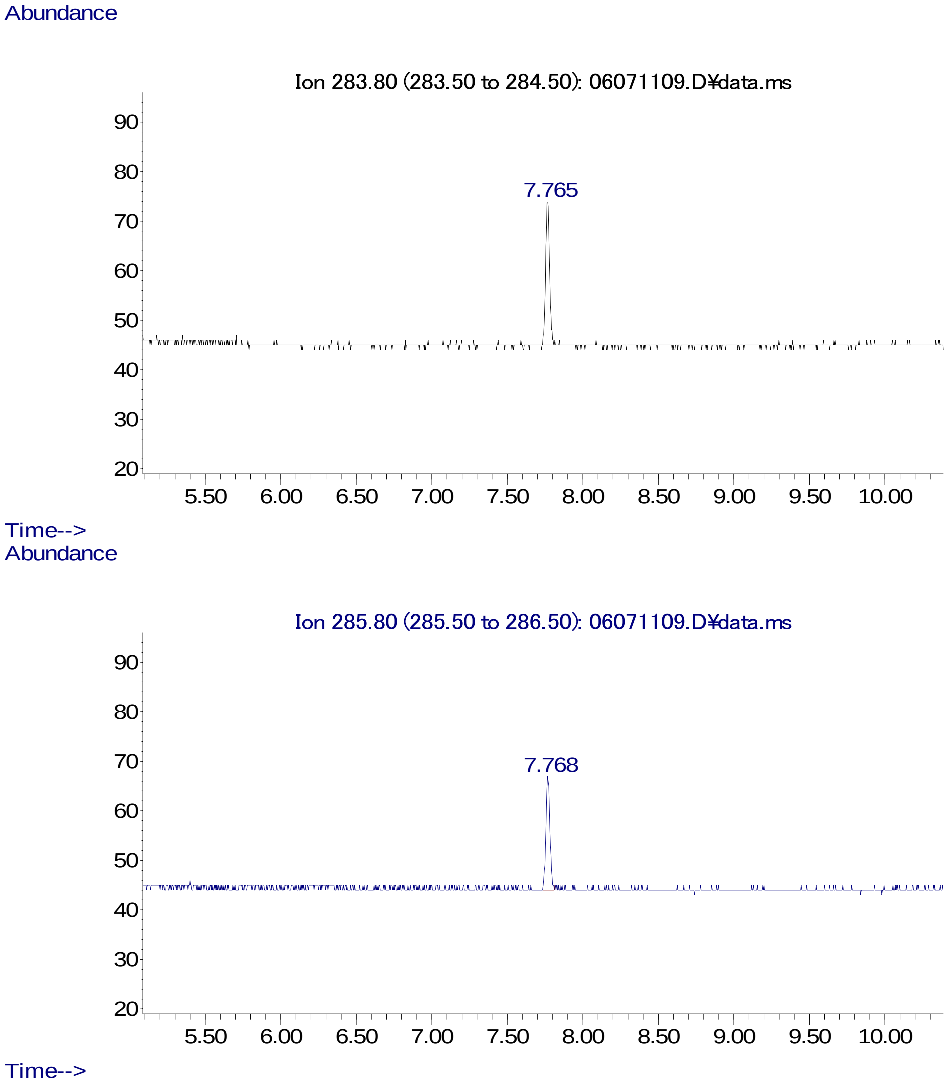
2. Calibration curve and detection limit

The calibration curve was prepared using the HCB peak area of the chromatogram obtained in the GS/MS (SIM) measurement of the standard solution. As shown in Figure 2, the good linearity was obtained within a range from 0.5ng/mL to 1000ng/mL.



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 an value tenfold of the standard deviation from the HCB peak area obtained from the measurement results of the standard solution for the calibration curve (0.5ng/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 100 mL) produced the quantitation limit of 2.8ppm, roughly one-seventieth of the BAT level (200ppm), 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 concentration (0.5ng/mL).

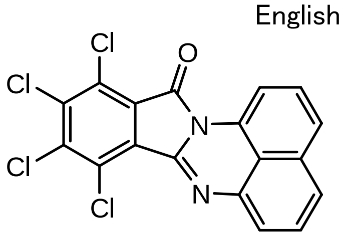
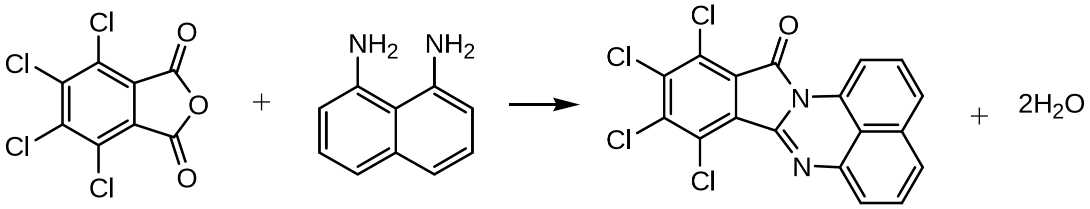


Ⅵ. Conclusion

1) An analysis of a sample dissolved with acetone found a favorable separation of TCPA and HCB, showing that it is fully possible to analyze HCB without purification.
2) The quantitation limit of this analytical method was 2.8ppm.

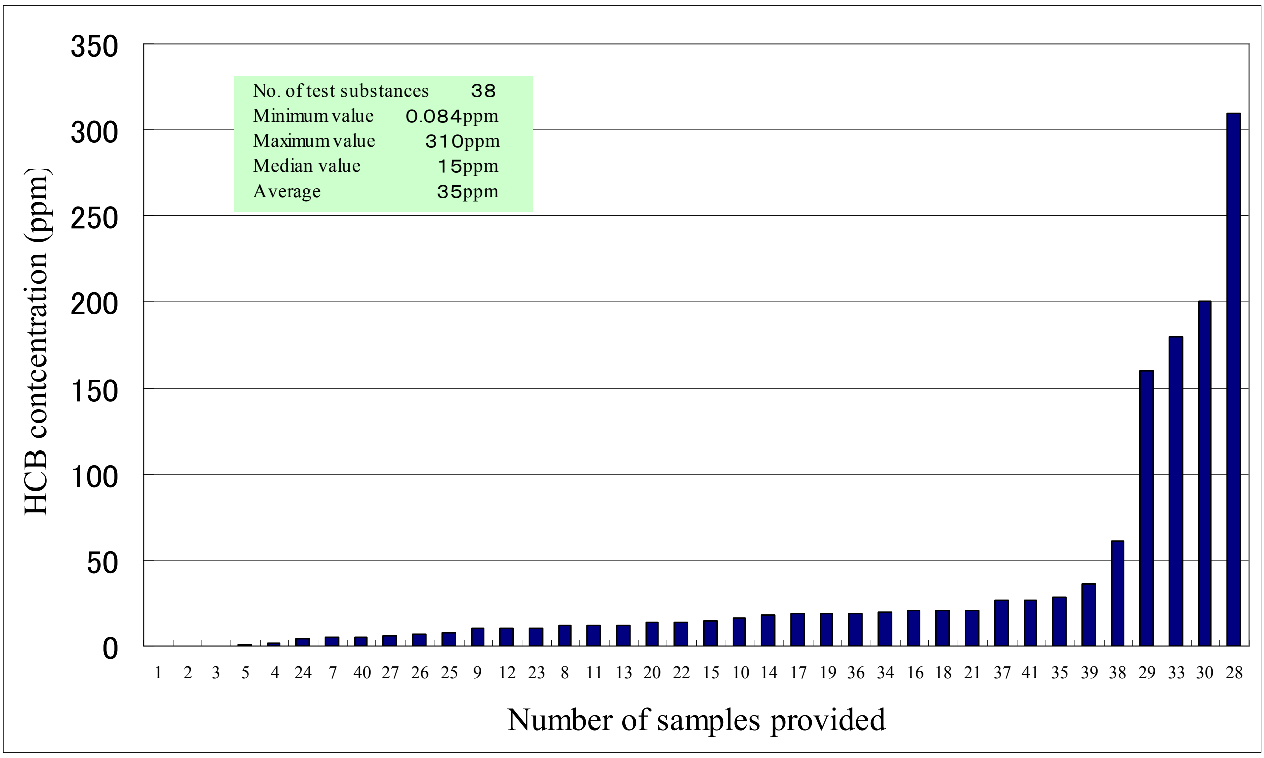
【Annex 8】

Description of Solvent Red 135

1	Structural formula	
	 English name: 8,9,10,11-tetrachloro-12H-phthaloperin-12-one CAS registration number: 20749-68-2	
2	Composition formula	$C_{18}H_6Cl_4N_2O$
3	Molecular weight	408.06
4	Law concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture,	
	Category	Existing
	Official Gazette publication reference number	5-3098
	Existing list Official Gazette publication name	Solvent Red－135
5	Physicochemical property (provided by manufacturer MSDS)	
	Appearance	Red micronized powder
	Density	About 1.1g/cm^3-1.8g/cm^3
	Melting point	306-318℃
	Boiling point	-
	Vapor pressure	-
	Water solubility	Not soluble in water
6	Solubility in organic solvents (g/100g-Solvent) (provided by manufacturer MSDS)	
	methanol	Almost insoluble
	butanol	Almost insoluble
	MEK	0.2%
	Xylene	0.2%
7	Manufacturing methods	
	(a) Add 1,8-Naphthalenediamine to tetrachlorophthalic anhydride, dissolve this in an organic solvent and raise temperatures to obtain a reaction, (b) After cooling it off, cleanse the crystallization to be separated by an organic solvent, and (c) After hot-water dispersion and cleansing, obtain the product by drying it. 	

【Annex 9】

HCB Concentration in Solvent Red 135 Provided by Companies (Results of Analysis by the Government)



【Annex 10】

Example of Measurement of HCB Content in Solvent Red 135 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 0.25mm, length 30m, 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: 1µL (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

0.01g of a sample was dissolved in sulfuric acid for a constant volume of 50mL. Then, 1mL was taken out to which 4mL 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 1mL for the cleanup using silica gel cartridges (Spelclean made by Supelco, LC-Si 6mL Glass Tube, 1g). After concentrating 10mL 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

The quantitative determination was made by obtaining the HCB peak area through the GC/MS (SIM) measurement. Confirmation was made in the SIM measurement by comparing the relative intensity ratio of qualitative ion with standard solution.

1 μL of sample solution was taken out to be injected 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 the SIM chromatogram for an analysis of HCB in the Solvent Red 135 sample.

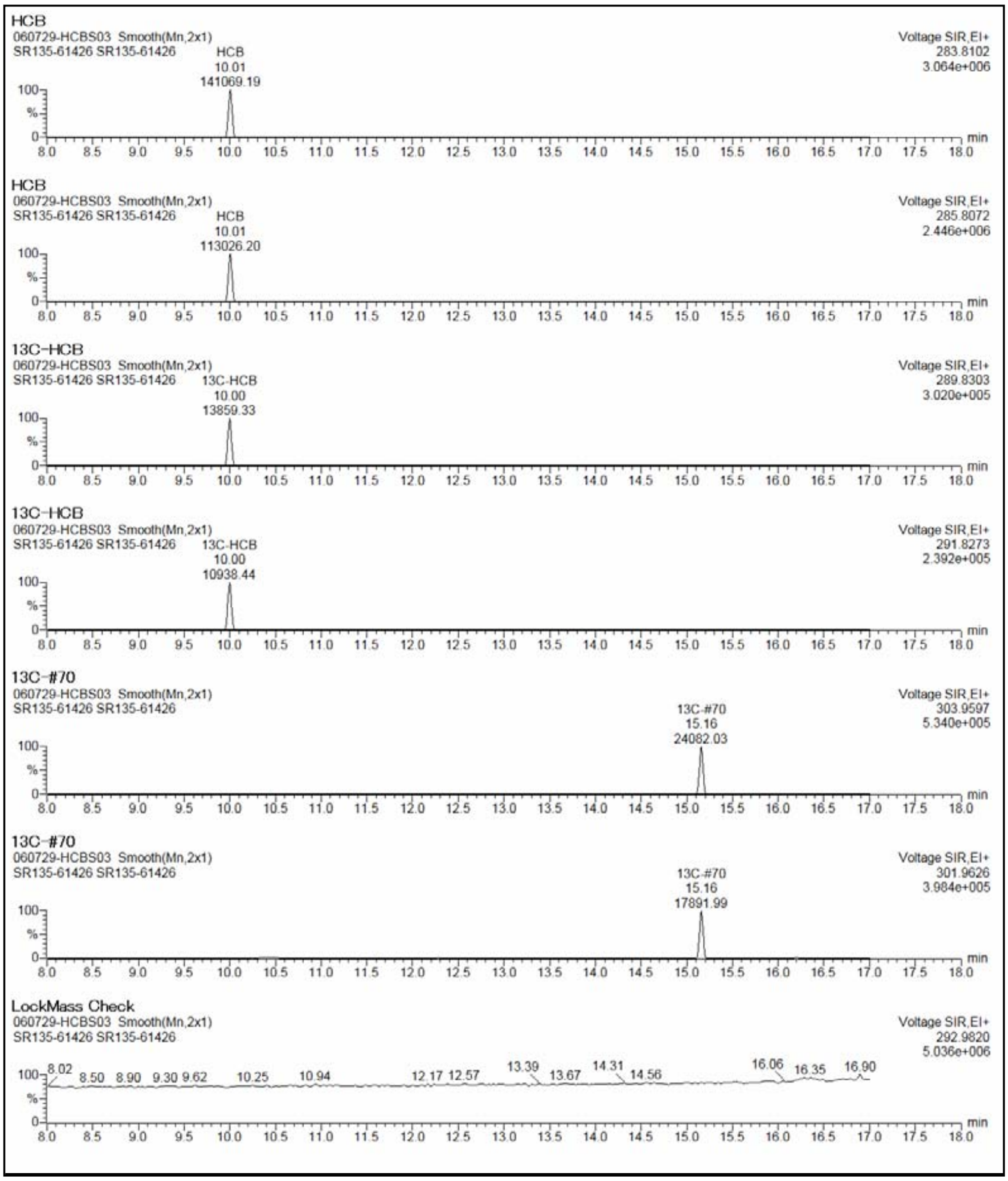


Figure 1 SIM Chromatogram for an Analysis of HCB in Solvent Red 135 Sample

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).

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

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.

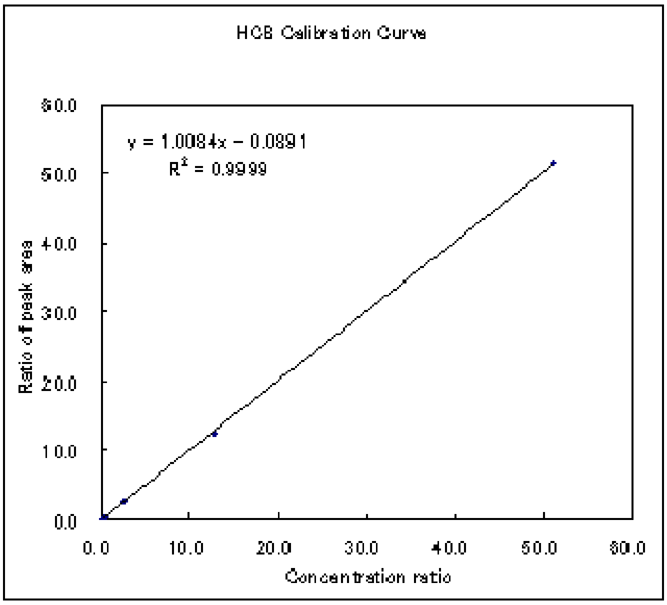


Figure 2 HCB Calibration Curve

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 (0.5ng/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 0.08μg/g, roughly one-125th of the BAT level (10ppm), 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 (0.5ng/mL).

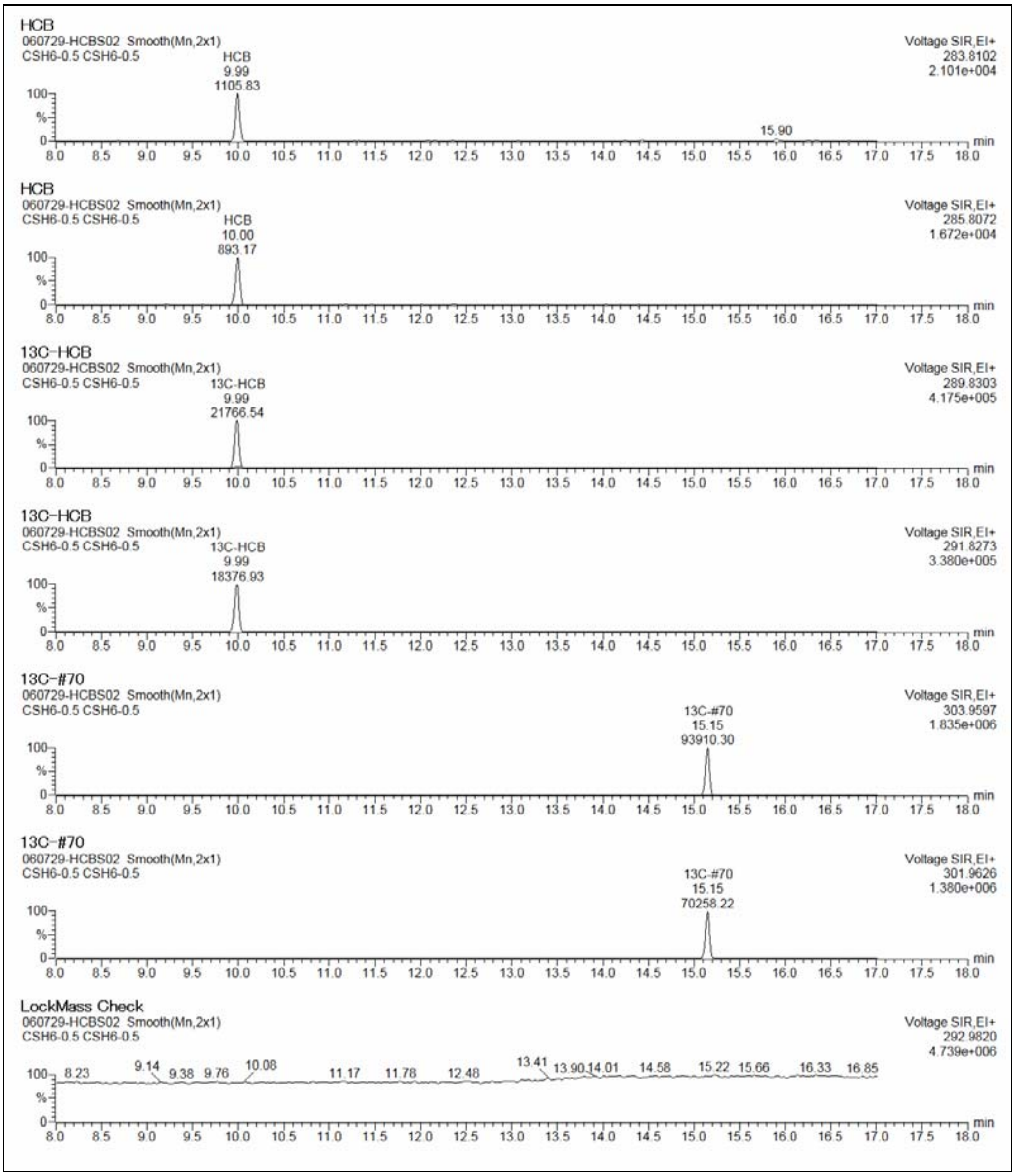


Figure 3 SIM Chromatogram of the standard solution for the calibration Curve with the Lowest Condensation

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.

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

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.

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

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 0.08ppm.