【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.

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

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

(snip)

【Annex 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) 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】

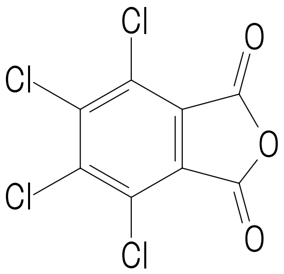
Committee Meetings

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	1.49g/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		

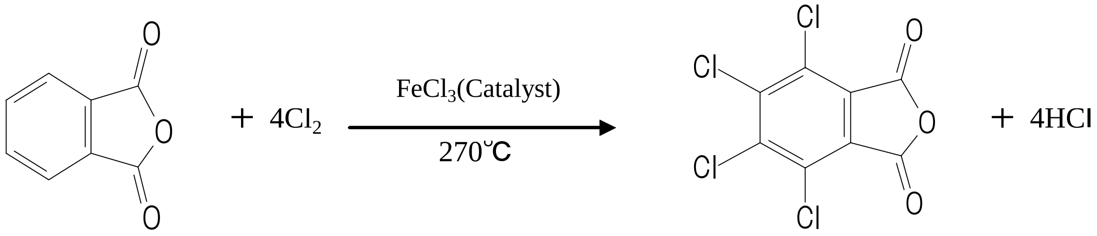
Domestic shipments: about 107 tons (the average for 1996-2005)

about 30 tons (actual for 2005)）

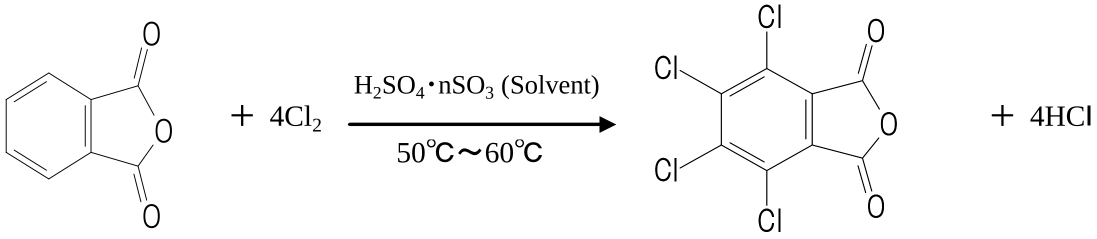
TCPA Manufacturing Method

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)

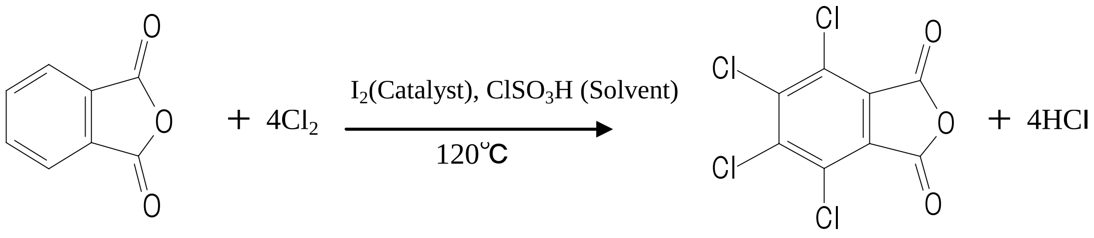
2 Method to cause a gas phase reaction between phthalic anhydride and chlorine gas with ferric chloride as a catalyst (Gas phase method)



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

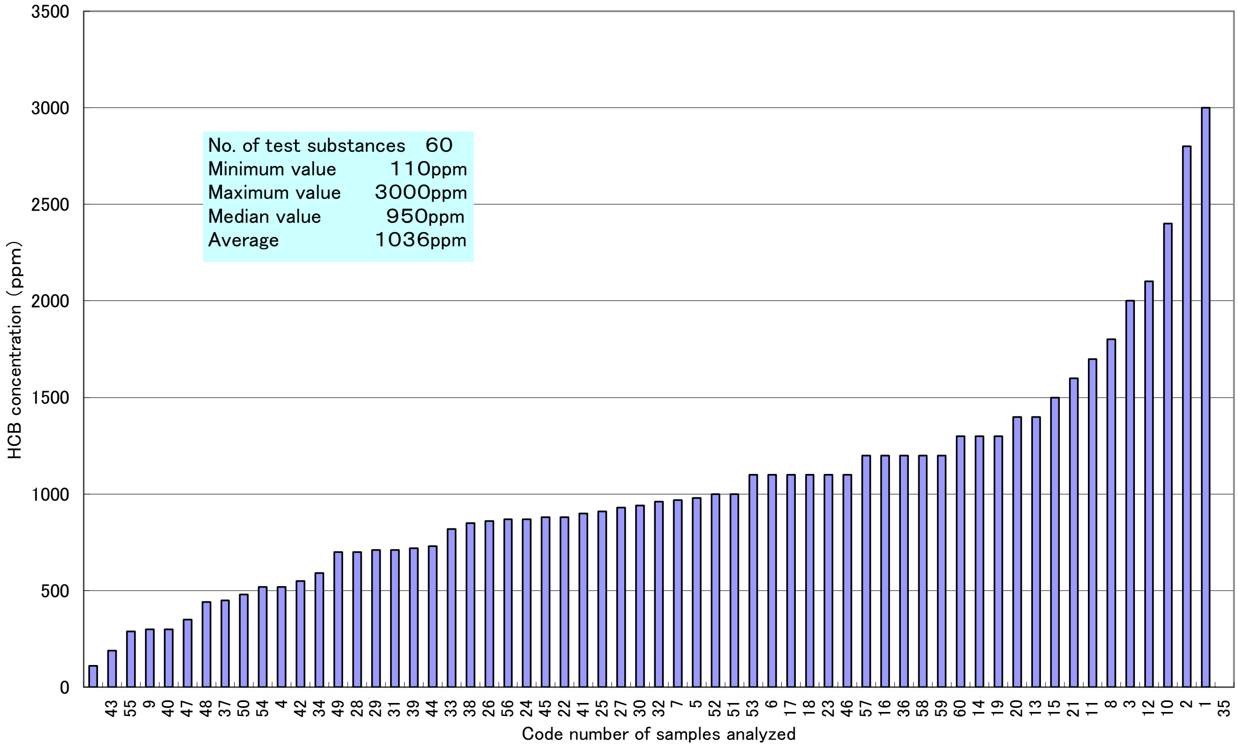


4 Method to cause a solution phase reaction between phthalic anhydride and chlorine gas using chlorine gas as a solvent and also using inactive chlorosulphonic acid as hydrochloric gas generated (Liquid phase method)
(Example)
Main raw material: phthalic anhydride, chlorine
Secondary raw material: chlorosulphonic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



【Annex 6】

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



No. of test substances	60
Minimum value	110ppm
Maximum value	3000ppm
Median value	950ppm
Average	1036ppm

【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.

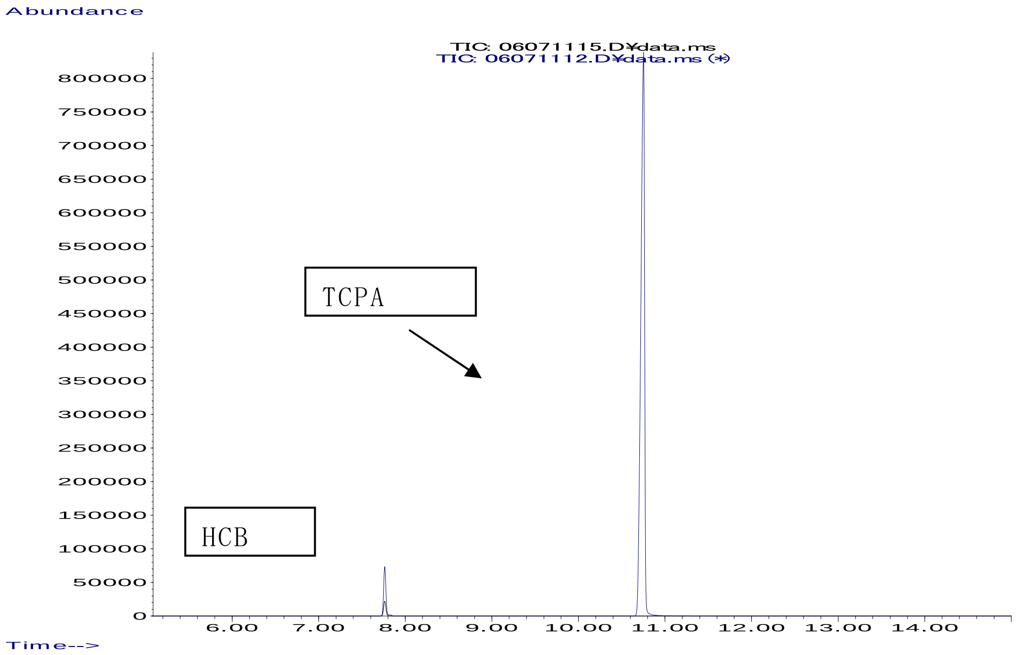


Figure 1 Chromatogram of TCPA Samples

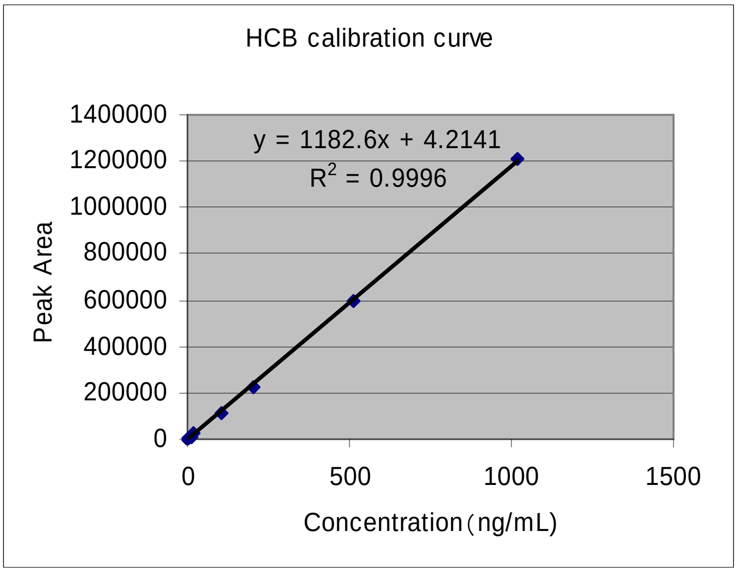
V. Results and Discussion

1. Consideration of analysis conditions

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

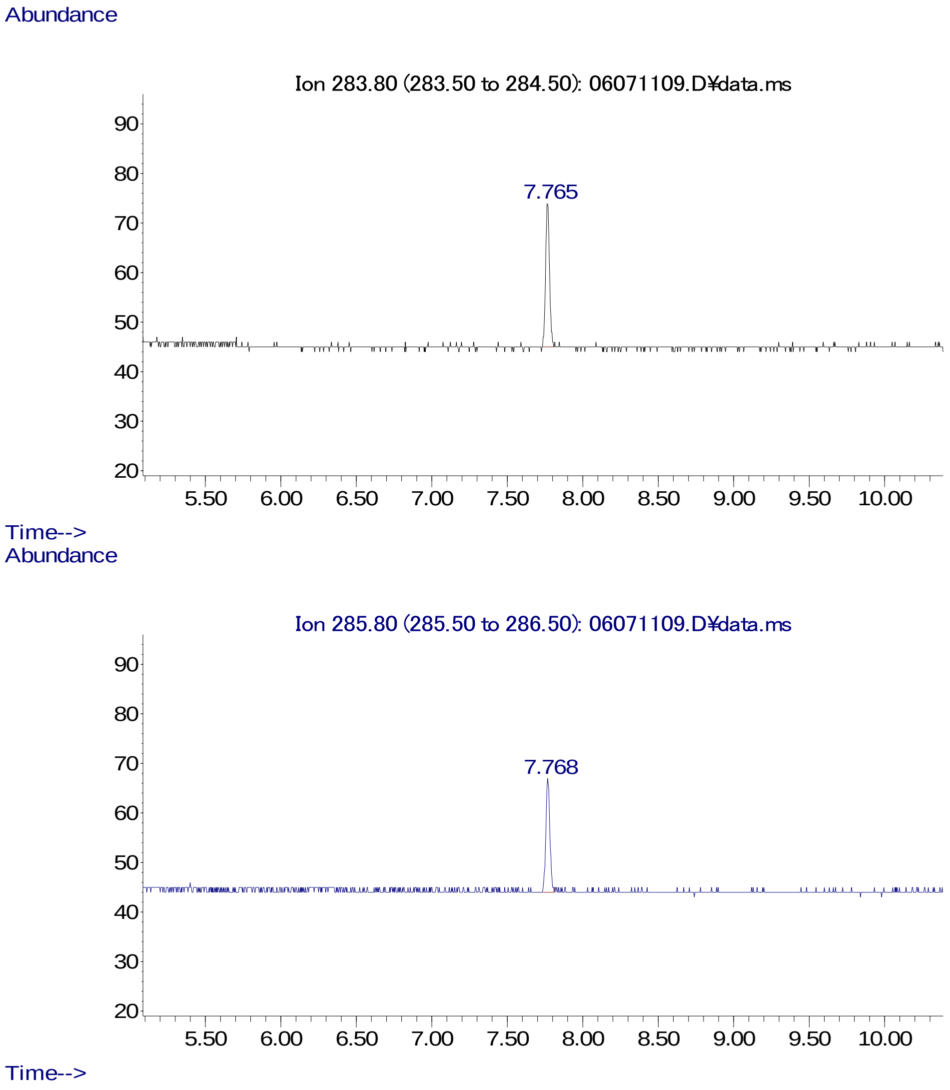
2. Calibration curve and detection limit

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).



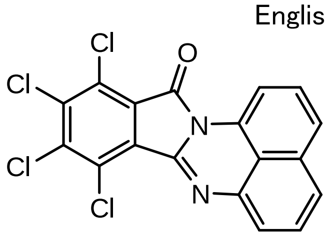
Ⅵ. Conclusion

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】

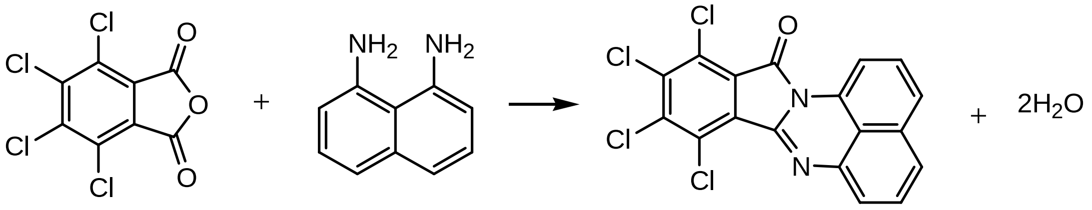
Description of Solvent Red 135

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,

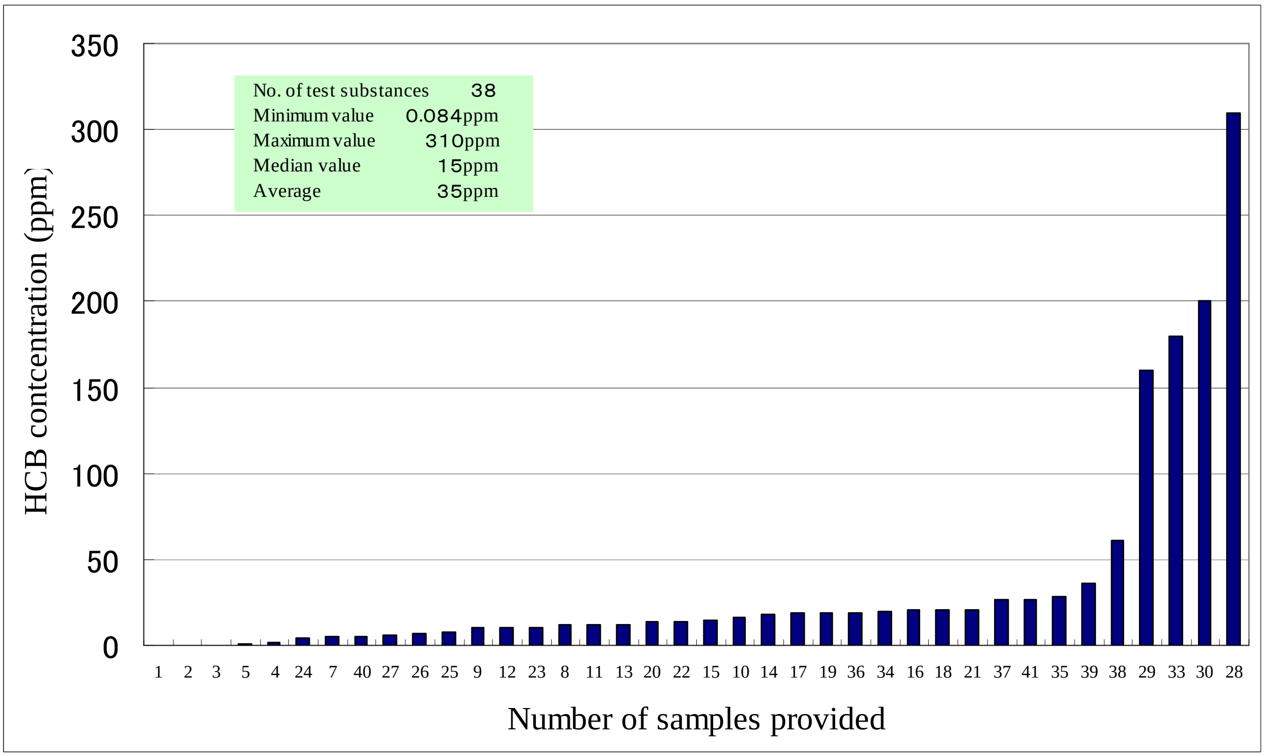
(b) After cooling it off, cleanse the crystallization to be separated by an organic solvent, and

(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.

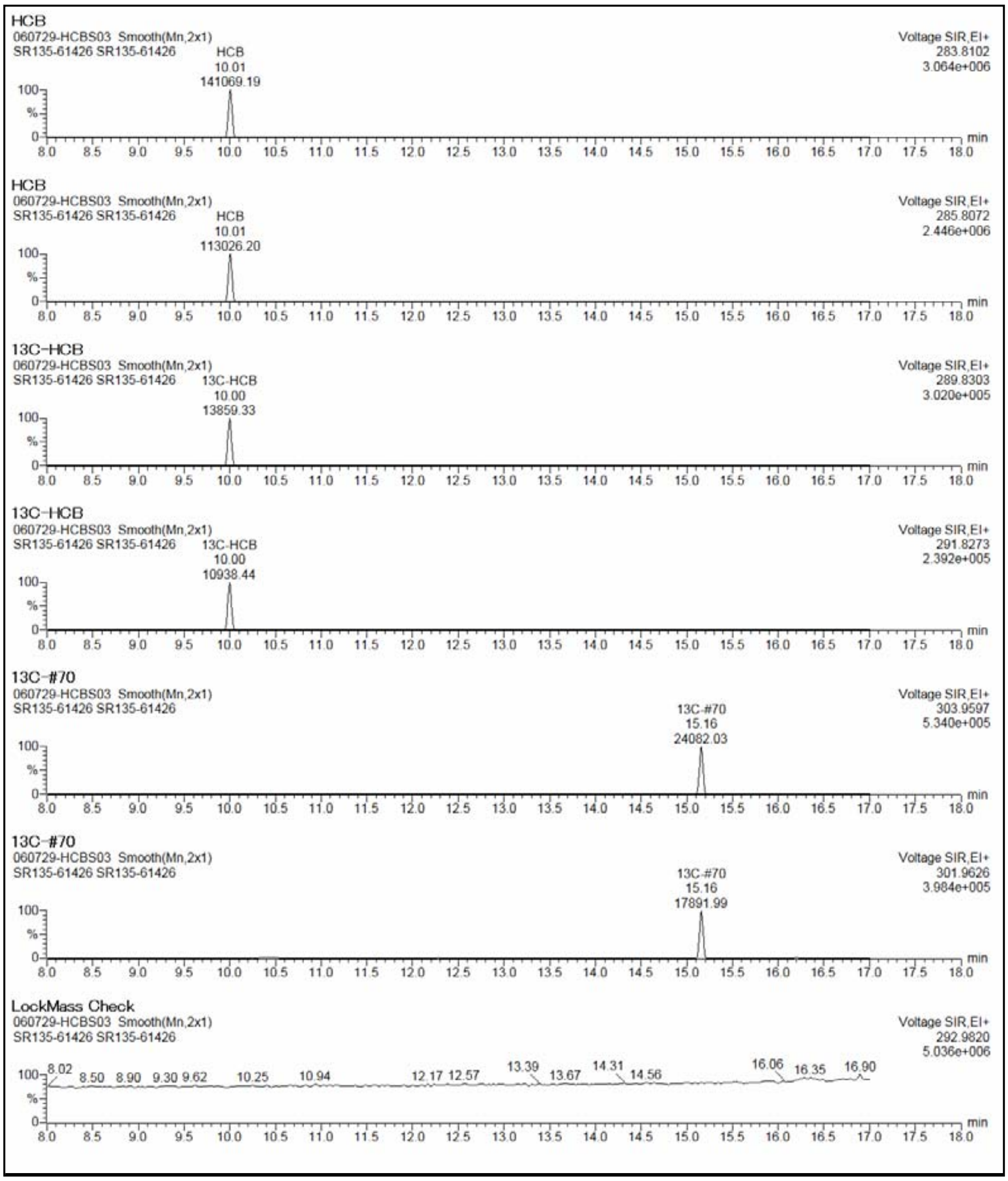


Figure 1 SIM Chromatogram for an Analysis of HCB in Solvent Red 135 Sample

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).

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

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

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

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

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

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

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

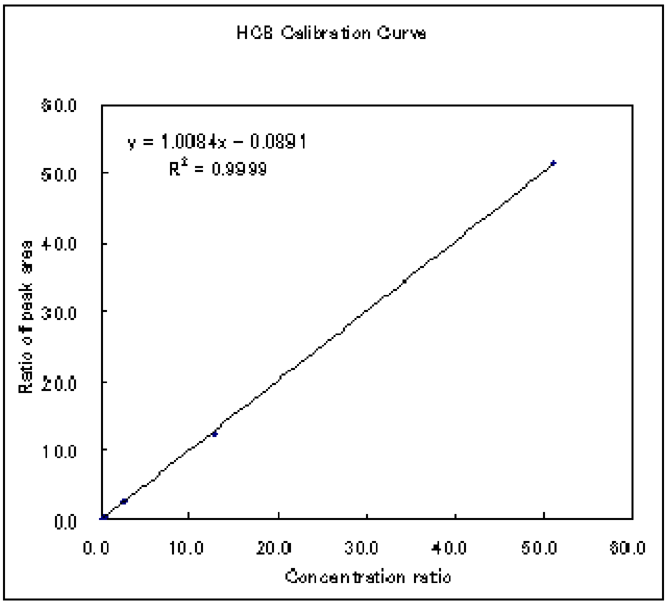


Figure 2 HCB Calibration Curve

The RRF calculation results are shown in Table 2.

Table 2 Results of RRF Calculation

Standard solution (ng/mL)	RRF
1020	0.907
255	0.876
51	0.905

5.1	0.939
0.51	0.872
Average RRF	0.89980
Standard deviation	0.02718
CV (%)	3.0

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

The quantitation limit was estimated with the use of the standard solution for preparing the calibration curve with the lowest HCB concentration substantially lower than one-tenth the BAT level. The quantitation limit was obtained as a value 10 times the standard deviation from the HCB peak area obtained from the measurement results of the sample solution for the calibration curve (0.5ng/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).

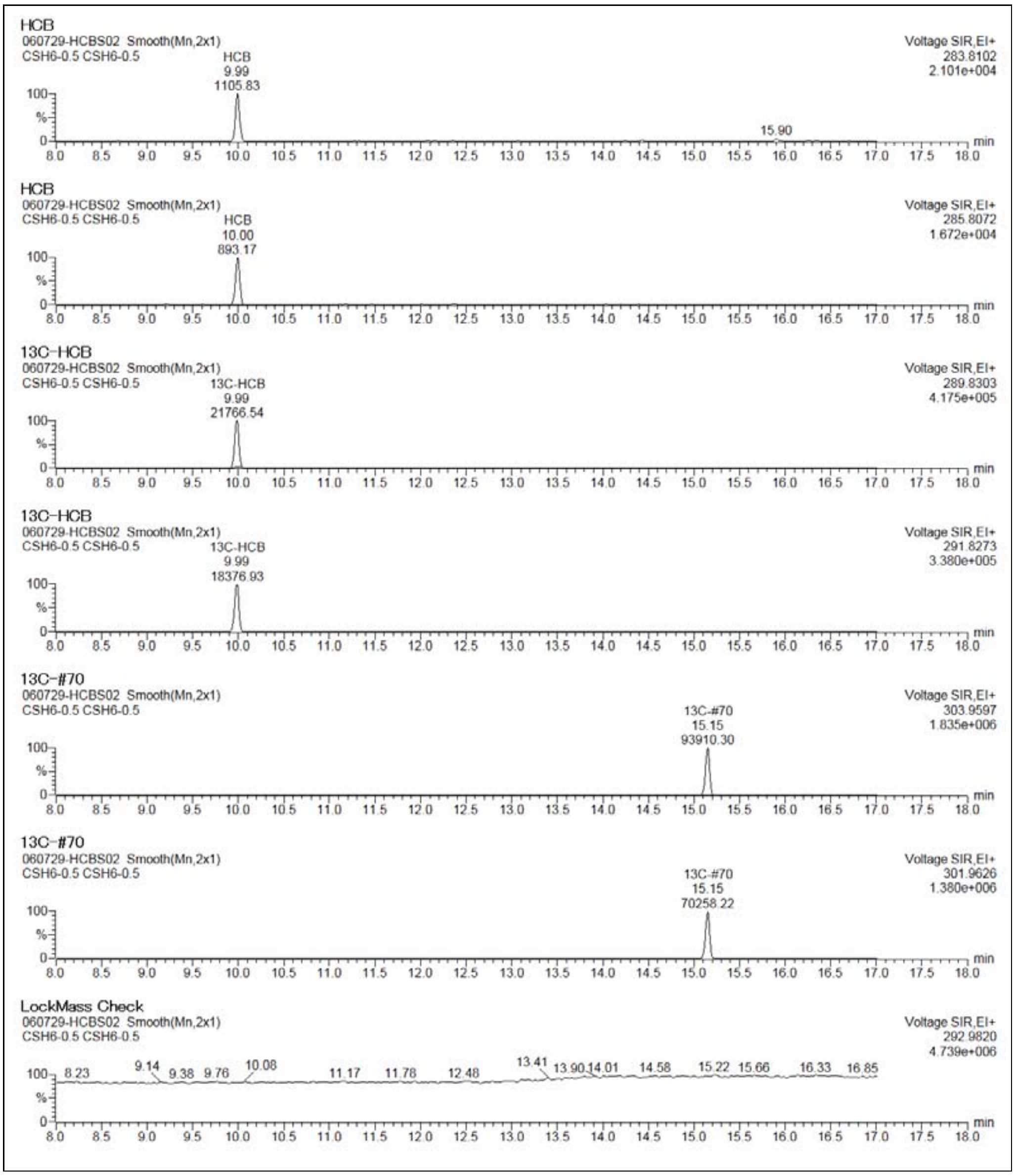


Figure 3 SIM Chromatogram of the standard solution for the calibration Curve with the Lowest Condensation

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.

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

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.

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

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.