

Thermal desorption GC/MS analysis method for PCBs in organic pigments 2

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Introduction

By notification the Ministry of Economy, Trade and Industry, the Ministry of the Environment, and the Ministry of Health, Labor and Welfare in March 2017, suppliers who newly manufacture or import organic pigments that meet certain condition have confirmed the concentration of the PCB produced as a by-product, and are required to explain the management method including the voluntary upper limit, analysis method, and analysis frequency. Therefore, the need for PCB analysis in organic pigments is increasing more and more. We reported thermal development of desorption GC/MS analysis method for PCBs in organic pigments as a screening method.¹⁾ In this method, it is possible to analyze by simply collecting 0.1 to 1.0 mg of organic pigment in a glass micro vial and setting it in the GC injection port, so it is possible easily to obtain the analysis without performing complicated pretreatment. In this report, we analyzed four organic pigments of phthalocyanine type, disazo type, pyrazolone type, dioxazine type, and we obtained the same PCBs composition pattern as the result of conventional method (hexane dispersion - sulfuric acid solution - hexane extraction - GC / HRMS analysis method)²⁾³⁾. However, since it was not comparing the same samples, we couldn't evaluate quantitative comparison. Therefore, the purpose of this study is comparing the quantitative value of thermal desorption GC/MS analysis method to one of the conventional method. In addition, we also tried to shorten the GC / MS analysis time by using the VF Rapid-MS PCB screen column for fast PCB analysis. Furthermore, we carried out the analysis using triple quadrupole GC/MS (GC/MS/MS) with higher selectivity because we found there are samples in which the influence of matrix was seen using single quadrupole GC/MS.

Materials and methods

The analysis flow chart is shown in Fig.1, and the GC / MS / MS equipment condition is shown in Table 1. For the thermal desorption, a thermal separation probe (TSP) made by Agilent was used in the same way as our previous report, and a temperature programmable GC inlet was used. For the analytical column, a VF Rapid-MS PCB screen column which is a wide bore analysis column (10m, 0.53mm, 0.25 μ m) combined pre-restrictor (0.6m, 0.1mm) was used. This column is a column for fast PCB analysis, which can elute all PCB congeners of three Arochlor within 4 minutes have been reported.⁴⁾ In addition, EC-5433 manufactured by Cambridge Isotope Laboratories was used as a calibration curve standard solution. The ranges of concentration of calibration curves were 10-1000 pg for 1-2 chlorinated congeners and 20-2000 pg for 3-10 chlorinated congeners. When it deviates from this calibration curve range, quantification was performed by extrapolation. Three kinds of samples, the phthalocyanine type (color index (CI): PG 7), disazo type (CI: PY 81), and pyrazosone type (CI: PO 13) were examined. The quantitative values of these samples are calculated by the conventional method. Agilent 7010 triple quadrupole MS was used for GC/MS/MS.

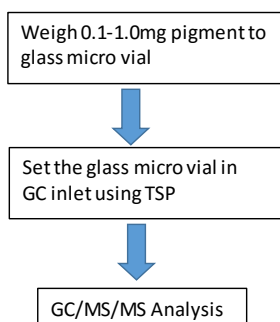


Fig.1 Flowchart of the screening method

Table1 GC/MS/MS run conditions

GC run condition	
Instrument	Agilent 7890B Gas Chromatograph
Column	VF Rapid-MS PCB screen column 0.1mm×0.6m + 0.53mm×10m×0.25 μ m
Injection mode	Split 100:1
Inlet temperature	85°C (0min) -60°C/min-260°C (1min) -150°C/min-85°C
Oven program	60°C (3min) -25°C/min-85°C (1min) -40°C/min-305°C(3min)
Carrier gas	Helium, 1.0mL/min, constant flow mode
MS condition	
Instrument	Agilent 7010 Triple Quadrupole
Acquisition parameter	EI mode; multiple reaction monitoring (MRM)
Collision gas	Nitrogen, 1.5mL/min
Quench gas	Helium, 1.5mL/min
MS temperature	Source 280°C, Quadrupole 150°C

Results and discussion

In the present analysis using VF Rapid-MS PCB screen column, the retention time of the last eluting PCB # 209 was 9.76 minutes including the thermal desorption time of 4 minutes. Therefore, the analysis time could be shortened to about 1/5 of 47.24 minutes of our previous analysis time using HT8-PCB column. #11 in the pyrazolone pigment (PO 13), #52 in the disazo pigment (PY 81) and #209 in the phthalocyanine pigment (PG 7) were detected as the major congeners in the same as our previous report. (Fig.2-4).

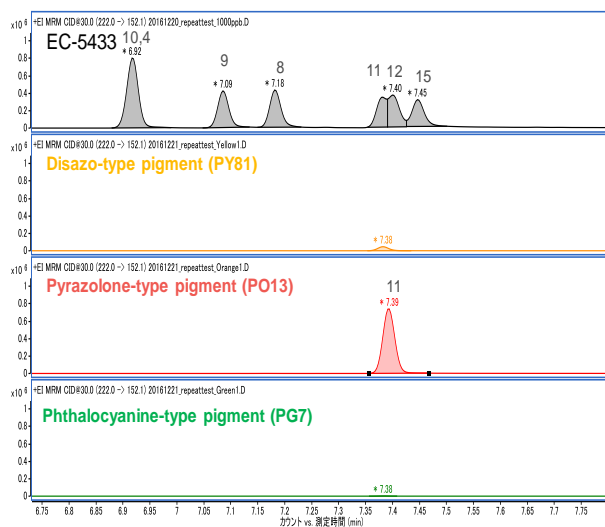


Fig.2 MRM chromatogram of #11 (Transition m/z 222.0→152.1)

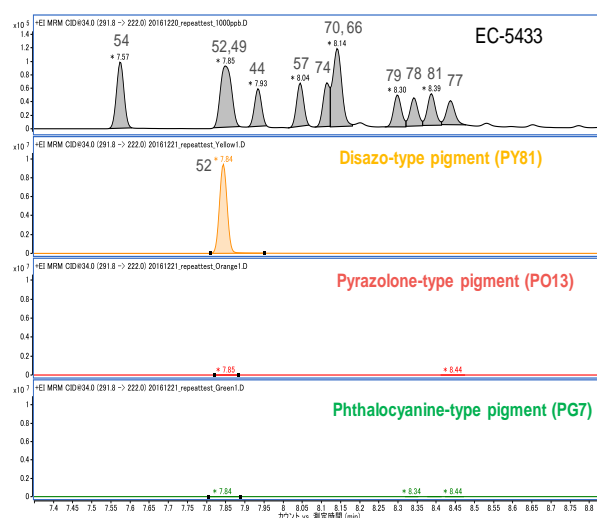


Fig.3 MRM chromatogram of #52 (Transition m/z 291.8→222.0)

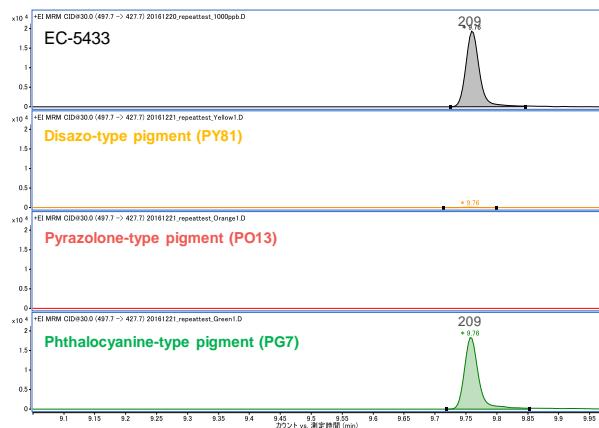


Fig.4 MRM chromatogram of #209 (Transition m/z 497.7→427.7)

Figures 5, 6 show bar charts with error bar comparing the quantitative value determined by this screening method ($n=3$) to the value of conventional method for # 209 of phthalocyanine pigment (PG 7) and # 52 of disazo pigment (PY 81). The result of # 209 the phthalocyanine pigment is as follow; the conventional method: 2.3 ppm, the screening method: 2.5ppm. The result of # 52 the disazo pigment is as follow; conventional method: 730 ppm, the screening method: 781 ppm. Therefore, for these two organic pigments, the screening method has the same quantitative value as the conventional method. On the other hand, for # 11 of pyrazolone pigment (PO 13), the quantitative value of this screening method was 3 times higher than the conventional method. Assuming the reason for high quantitative value is heat generation during thermal desorption, analysis of pyrazolone pigment at low heat desorption temperature was investigated. Fig.7 shows normalized area of #11 in pyrazolone pigment at various desorption temperature. Since a sharp increase in area value was observed in the range from 230 ° C to 260 ° C, it was considered that 230 ° C or less is better. In addition, since approximately the same relative peak area value was obtained at thermal desorption temperatures of 170, 185 and 200 ° C, it was ultimately decided to 185 ° C. Fig.8 shows bar graph with error bar comparing the quantitative value determined by the changed screening method ($n=3$) to the value of conventional method for # 11 of pyrazolone pigment (PO13). The result is as follow; the conventional method: 9.4 ppm, the screening method: 5.3 ppm. Since the quantitative value of the screening method became close to the value of the conventional method, it was considered that the desorption temperature of 185 ° C is an appropriate temperature.

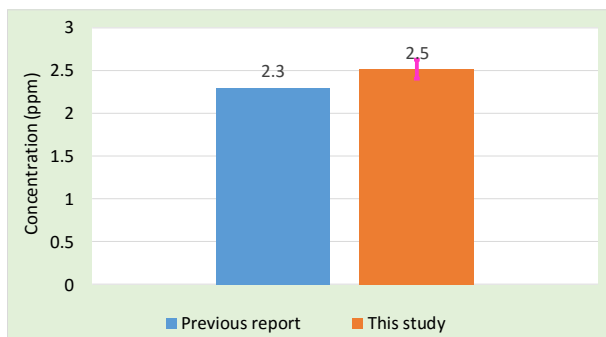


Fig.5 Comparison of concentration of #209 in phthalocyanine-type pigment between previous report and this study

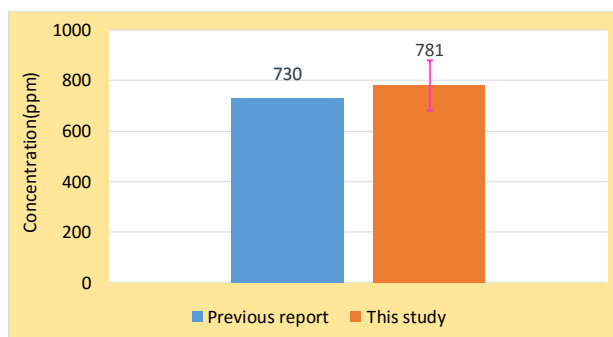


Fig.6 Comparison of concentration of #52 in disazo-type pigment between previous report and this study

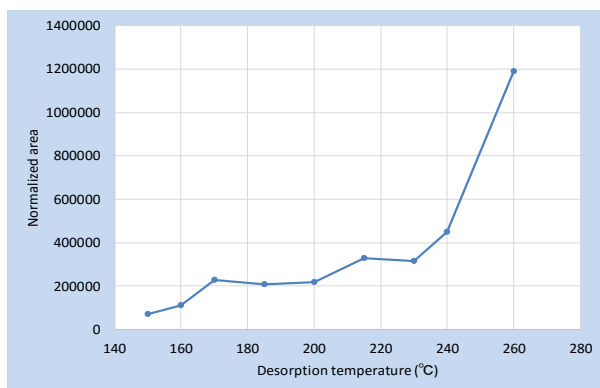


Fig.7 Normalized area of #11 in pyrazolone-type pigment at various desorption temperature

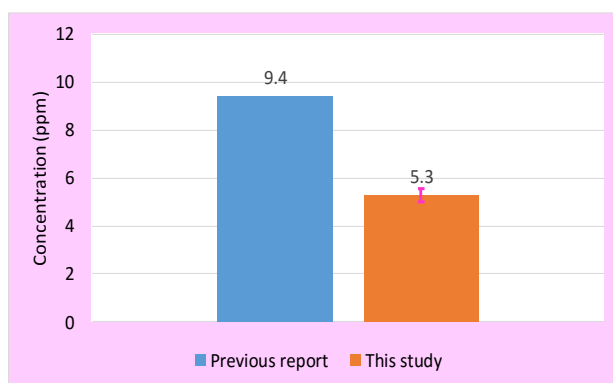


Fig.8 Comparison of concentration of #11 in pyrazolone-type pigment between previous report and this study

References

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