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Report

Study Title

Migration test of 9,10-anthraquinone in the Unbleached kraft paper

Food simulant E : poly(2,6-diphenyl-p-phenylene oxide)

Study Director

[redacted]

Study Completion Date

February 13, 2014

Test Facility

Sumika Chemical Analysis Service, Ltd.

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Study Number

8369129-00

Sponsor

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1. Aim of the study

The Aim of the study is to perform migration test of 9,10-anthraquinone(AQ) in the Unbleached kraft paper in accordance with the COMMISSION REGURATION (EU) No 10/2011.

2. Samples and analyte assayed

2.1. Samples

The following samples were provided by the sponsor:

(1) Unbleached kraft paper (A)

Paper (A): Basis weight is 81g/m^2, AQ content is 5.7ppm.

(2) Unbleached kraft paper (B)

Paper (B): Basis weight is 81g/m^2, AQ content is 1.6ppm.

2.2. Analyte assayed

Chemical name	: 9,10-anthraquinone (AQ)
Molecular formula	: $C_{14}H_8O_2$
Molecular weight	: 208
CAS No.	: 84-65-1

3. Summary

Sample name	Food simulant
	E : poly(2,6-diphenyl-p-phenylene oxide) (μg/dm²)
Paper (A)	<0.1*
Paper (B)	<0.1*
Objective limit of detection	<0.1*

* Concentration of AQ

* Value was calculated from the limit of detection.

4. Reagents

- Acetone
  : For pesticide residue and polychlorinated biphenyl analysis #300, Wako Pure Chemical Industries, Ltd.
- Dichloromethane
  : Special grade, Wako Pure Chemical Industries, Ltd.
- Toluene
  : HPLC grade, Wako Pure Chemical Industries, Ltd.
- poly(2,6-diphenyl-p-phenylene oxide)
  : TENAX, GL Sciences Inc.
- AQ
  : Purity >99%, Wako Pure Chemical Industries, Ltd.
- Anthraquinone-d8 (d8-AQ)
  : C/D/N ISOTOPES Inc.

5. Migration conditions

The migration conditions are shown below.

Food simulant	Migration time and temperature
E: TENAX	10 days at 60℃

The samples were exposed to TENAX in petri dish. According to BS-EN 14338, the ratio of sample surface area to volume of food simulant was $1dm^2/4g$. The migration tests were performed in double runs.

The blank test was prepared by the same procedure without using a sample.

The recovery test was prepared by the same procedure without using a sample with the addition of standard substance.

After migration tests, the sample solutions were prepared for the measurement. The preparation procedure was described in section 7.

6. Preparation of the standard solutions

6.1. Internal standard solutions

Approximately 0.01 g of d8-AQ was weighed into a 10 ml volumetric flask. The flask was added approximately 2mL of dichloromethane and it was filled up to the mark with toluene. The solution was diluted to approximately 0.1, 1.0 and 10 µg/mL with toluene.

6.2. Standard solutions

Approximately 0.01 g of AQ was weighed into a 10 ml volumetric flask. The flask was added approximately 2mL of dichloromethane and it was filled up to the mark with toluene.

For calibration curve, the solution was diluted to 0.005, 0.010, 0.020, 0.050 and 0.10µg/mL with toluene. At that time, internal standard solution was added to each solution to a concentration of approximately 0.050µg/mL. These solutions were measured in the condition of section 8.

For recover test, the solution was diluted to 10µg/mL with acetone.

7. Preparation of the sample solutions for measurement

All of TENAX prepared in section 5 and 70mL of acetone were placed in a vial and extracted with the ultrasonication for 10 minutes. Then the solution was filtrated and placed in a 100mL volumetric flask. The flask was filled up to the mark with acetone. 1mL of the solution and 50µL of internal standard solution (1µg/mL) were mixed well and measured in the condition of section 8.

8. Analysis conditions

The solutions prepared in section 6 and 7 were measured in the following conditions.

Apparatus (GC-MS)	: 6890N-5973N (Agilent Technologies)
Column	: DB-5ms (Agilent Technologies)
	30m x 0.25mm id, 0.25µm film thickness
Oven temperature	: 70 °C (1 min) - 10 °C /min - 300 °C (5min)
Injection volume	: 1 µL
Injection	: Pulsed splitless
Injection temp	: 300 °C
Carrier gas	: He, 1 ml/min, constant flow
Detector	: MSD, SIM
	m/z AQ:208, d8-AQ:216

9. Calculation

The amount of AQ in the sample solution was determined by comparison with calibration curve using the internal standard procedure.

The formula was below:

$$Y = aX + b$$

$$X = Aaq / A_{IS}$$

$$Y = Caq / C_{IC}$$

$$Caq = (a\ Aaq / A_{IS} + b)\ C_{IC}$$

where a : slope

b : y-intercept

Caq : Amount of the AQ

C_{IS} : Amount of the internal standard

Aaq : Peak area of the AQ

A_{IS} : Peak area of the internal standard

10. Results

The calibration curve data are shown in Table 1. The results of measurement of sample solutions are shown in Table 2. The results of recovery test are shown in Table 3. The calibration curve is shown in Fig.1. Chromatograms are shown in Fig.2-6.

11. Validation

Lower Limit of quantitation

The lower limit of quantitation (LLOQ) was 0.005 µg/mL. At that time, the signal to noise ratio (S/N ratio) was >10.

Limit of detection

The limit of detection was calculated from the chromatogram of 0.005 µg/mL standard solution measurement. It was 0.001 µg/mL. At that time, the signal to noise ratio (S/N ratio) was >3. This value was satisfied objective limit of detection in the food simulant.

Selectivity

The analysis method was found to be selective because no response was shown in the blank solution.

Accuracy

The analysis method was accepted because the average recovery of validation test was 100%.

Precision

The analysis method was accepted because percentage of difference of n=2 in recovery test was 1.1%.

Linearity

The calibration curve was accepted because the determination coefficient (R2) was >0.99.

12. Tables

Table 1 Calibration curve data

AQ Concentration (µg/mL)	Peak area	
	AQ	d8-AQ
0.005	8143	80728
0.010	16213	76414
0.020	30100	75587
0.050	78212	76907
0.10	153556	75627

Table 2 Results of measurement of the sample solutions

Sample name	n	Peak area		Amount of AQ / Surface area of sample (µg/dm²)	Average Amount of AQ / Surface area of sample (µg/dm²)
		AQ	d8-AQ		
Paper (A)	1	0	67141	< 0.1*	< 0.1*
	2	0	64782	< 0.1*	
Paper (B)	1	0	65496	< 0.1*	< 0.1*
	2	0	64655	< 0.1*	
Blank	1	0	63019	< 0.1*	< 0.1*
	2	0	66443	< 0.1*	

* Extrapolation value

* Value was calculated from the limit of detection.

Table 3 Results of recovery test

n	Peak area		Concentration in the extraction solution (μg/mL)	Amount in the extraction solution (μg)	Added amount (μg)	Recovery (%)	Average recovery (%)
	AQ	d8-AQ					
1	20900	64133	0.016	1.6	1.6	100	100
2	20678	64173	0.016	1.6	1.6	99	

13. Figures

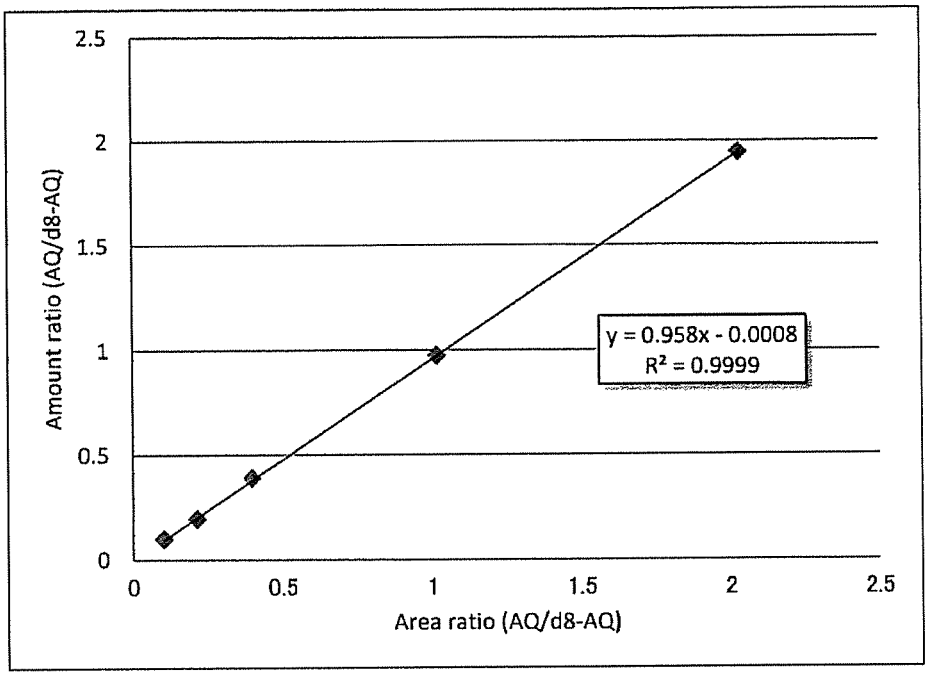

Fig.1 Calibration curve

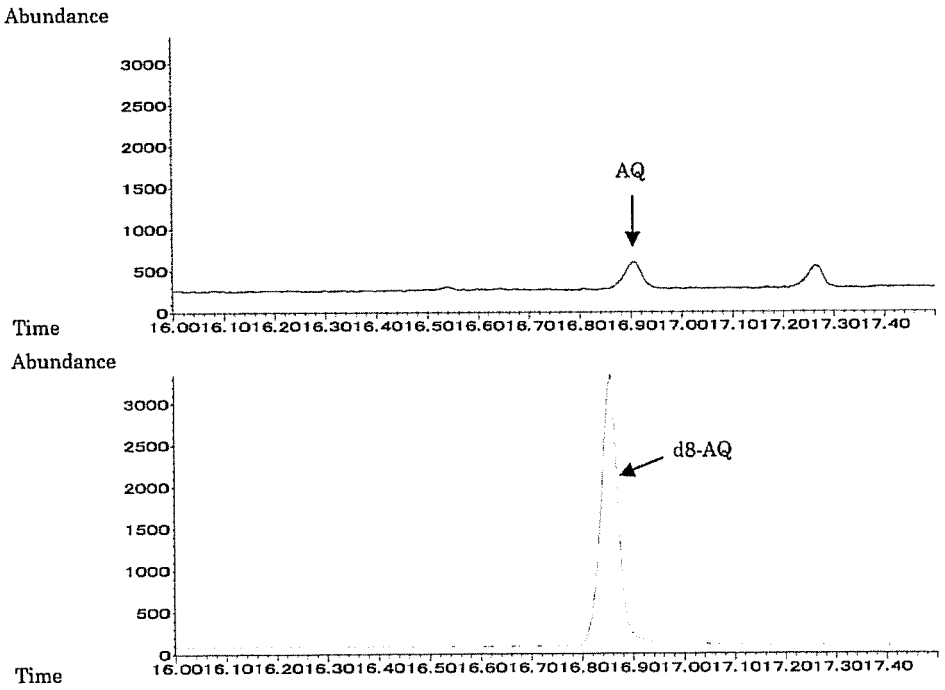

Fig.2 Typical chromatogram of standard solution (0.005μg /mL)

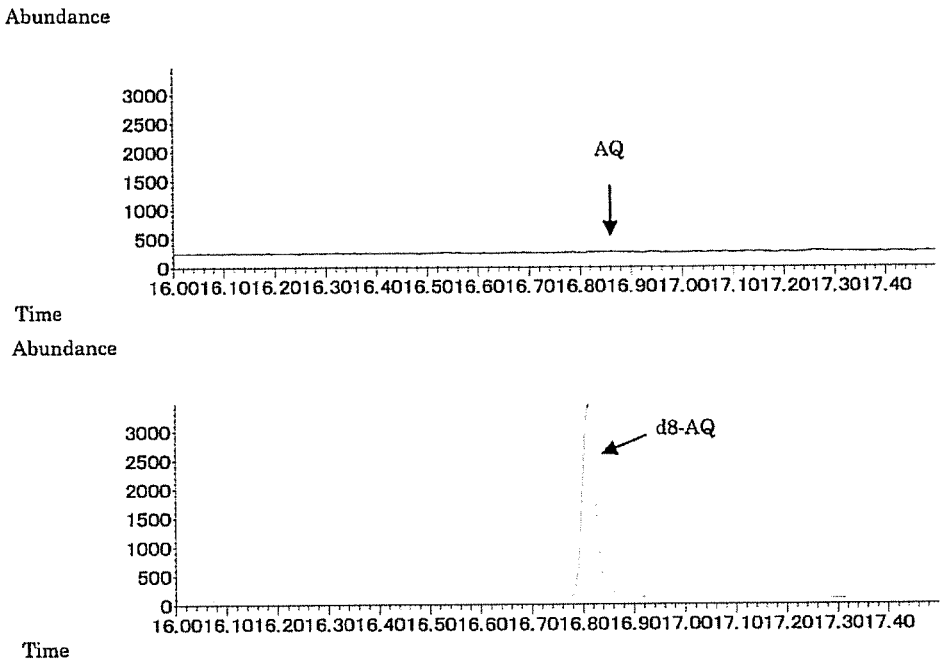

Fig.3 Typical chromatogram of blank solution

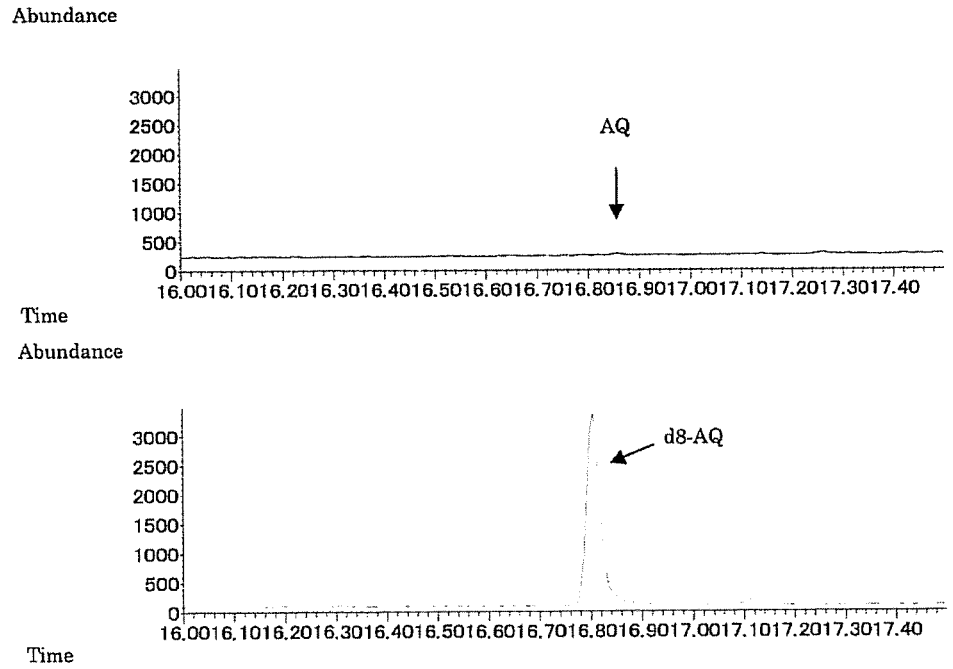

Fig.4 Typical chromatogram of Paper (A)

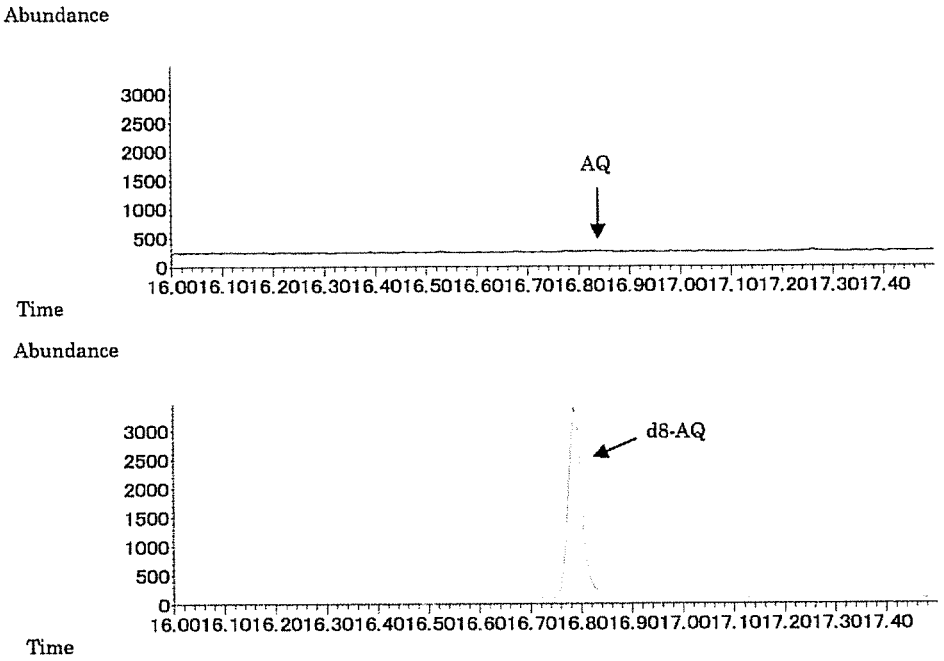

Fig.5 Typical chromatogram of Paper (B)

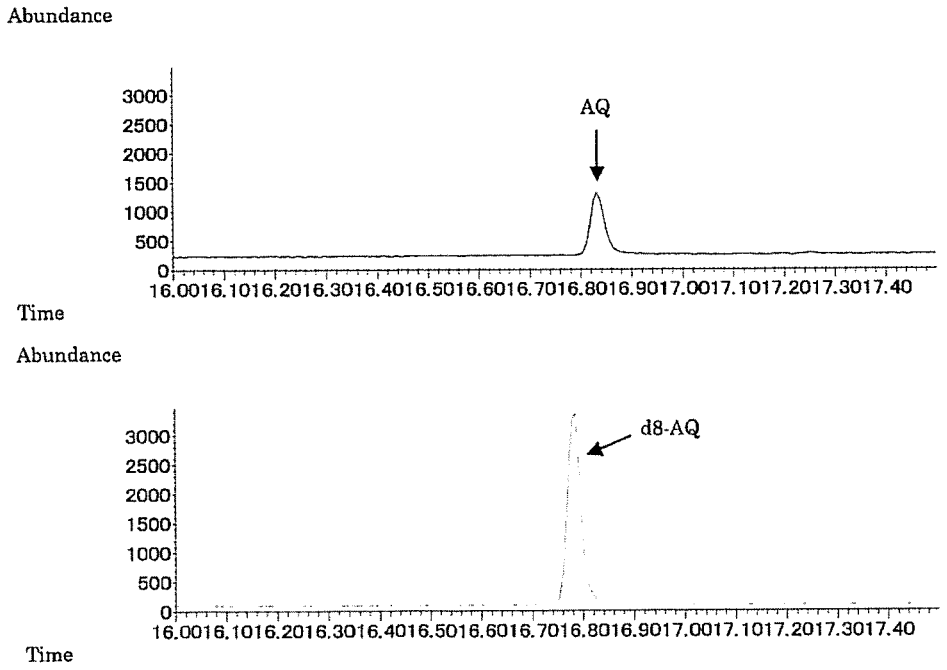

Fig.6 Typical chromatogram of recovery solution

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Discussions from the results of study (Study Number: 8369129-00)

The migration test of 9,10-anthraquinone (AQ) for the Unbleached kraft paper was performed in accordance with the COMMISSION REGURATION (EU) No.10/2011 and BS EN 14338:2003 "Paper and board intended to come into contact with foodstuffs – Conditions for determination of migration from paper and board using modified polyphenylene oxide (MPPO) as a simulant". The results of migration test using food simulant E (MPPO) according to BS EN 14338:2003 were less than 0.1μg/dm^2, which was calculated from the limit of detection. On the other hand, COMMISSION REGURATION (EU) No. 10/2011 provides that "the value of migration shall be expressed in mg/kg applying a surface to volume ratio of 6 dm^2 per kg of food". Therefore, the results of migration testing obtained in food simulant E (MPPO) can be expressed as less than 0.0006mg/kg-food (0.6ppb).

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