

Technical Requirement for Environmental Products

The Certificable Technical Requirement for Environmental Labelling Products

HBC 12—2002

Water Soluble Coating

Replace HJBZ 4—1999

1 Scope

This technical requirement specifies definition, basic requirement, technical content and test method for environmental labelling products of water soluble coating.

This technical requirement shall apply to various coatings and their products which use water as solvent or dispersion medium, such as water soluble wall coating, water soluble wood paint, water soluble water proofing paint, water soluble anti-corrosive paint, etc.

2 Standards cited

Provisions in the following standards are cited in this technical requirement, and therefore form the provisions in this standard. They have the same effectiveness as the technical requirement itself.

GB/T 1728-88 Methods of test for drying time of coatings of paints and putties

GB/T 1730-93 Determination of hardness of the paint films--Pendulum damping test

GB/T 1731-93 Determination of flexibility of films

GB/T 1732-93 Determination of impact resistance of film

GB/T 9286-88 Paints and varnishes Cross cut test for films

GB/T 18446-2001 Using gas chromatography to mensurate carbamate prepolymer and unreacted toluene diisocyanate (TDI) monomer in coatings solution

In case of the criteria above are revised, the latest version should be applied.

3 Definition

"Concentration of total volatile organic compounds (TVOC)" refers to, in special test conditions, content of all volatilizable organic compounds per volume of coating except water .

4 Basic requirements

4.1 Quality of products shall conform with the requirement of relevant product quality standards; physical chemical properties of water soluble wood paint shall meet requirement in 4.2.

4.2 Physical chemical properties of water soluble wood paint should accord with table 1.

Table 1 Physical chemical properties indexes for water soluble wood paint

Test items	Drying time, h		Adhesion, (square size 1mm), level	Flexibility, mm	Resistance to impact, cm	Hardness
	Dry tack free	Dry as a bone				
Limitation	1	3	≤2	≤ 2	≥45	≥0.36

4.3 Pollutant emission of the company should be obliged to conform with pollutant emission standards nationally or locally.

4.4 Substances harmful to human health such as halohydrocarbon, benzene, toluene, xylene, ethylbenzene, formaldehyde and their polymeric compounds should not be artificially used in production procedure.

Approved by SEPA on 03/15/2002

Entered into force on 03/15/2002

5 Technical contents

5.1 Benzene, toluene, xylene, ethylbenzene, halohydrocarbon, formaldehyde and polymeric compound of formaldehyde as well as heavy metal such as pb, Cd, Cr, mercuric compounds should not be used in products. Whereas limitation of hazardous substances carried by impurity should conform with requirement of tabel 1.

Table 1 Limitation for hazardous substances

Hazardous substances		Limitation, mg/kg
Benzene, toluene, xylene, ethylbenzene		500
Halohydrocarbon		500
Formaldehyde and its polymeric compounds		100
Heavy metal	Hg	60
	Pb	90
	Cd	75
	Cr	60

5.2 Content of free TDI monomer in hardener of water soluble polyurethane coating should not higher than 5000mg/kg.

5.3 Concentraion of TVOC in products should meet the requirements in table 2.

Table 2 Limitation of TVOC in water soluble coatings

Product category	Limitation for TVOC, g/L
Inner wall coating	100
External wall coating	200
Water soluble wood paint, water soluble anti-corrosive paint, water soluble water proofing paint	250

6 Test

6.1 Test for content of TVOC in products should be conducted according to annex A.

6.2 Formaldehyde content in product should be conducted according to annex B.

6.3 Heavy metal content in product should be conducted according to annex C.

6.4 Test for adhesion of water soluble wood paint should be conducted according to the method specified in GB/T 9286-88.

6.5 Test for flexibility of water soluble wood paint should be conducted according to the method specified in GB/T 1731-93.

6.6 Test for resistance to impact of water soluble wood paint should be conducted according to the method specified in GB/T 1732-93.

6.7 Test for hardness of water soluble wood paint should be conducted according to the method specified in GB/T 1730-93.

6.8 Test for drying time of water soluble wood paint should be conducted according to the method specified in GB/T 1728-88.

6.9 Test for contents of halohydrocarbon, benzene, toluene, xylene, ethylbenzene in products should accord with annex D.

6.10 Test for free TDI monomery in polyurethane coating should be conducted according to annex A in GB/T 18446-2001.

Annotations:

This technical requirement has been prepared by Department of science and technology, standards of State Environment Protection Administration.

The State Environment Protection Administration keeps the right of interpretation for this technical requirement.

Annex A Determination of TVOC content in water soluble coating

Part One: Determination for total volatile substances in water soluble coating

A.1 Test conditions

Instrument, equipment

Analytical balance: weighing accuracy $\pm 0.0001\text{g}$;

Aluminum foil tray: 58mm in diameter, 18mm high;

Oven;

Syringe: 1.0ml

A.2 Measuring method

Weigh sample aliquot depending on content of volatile matter in water soluble coating:

If content of volatile matter is $< 40\%$, weigh aliquot $0.3 \pm 0.1\text{g}$;

If content of volatile matter is $> 40\%$, weigh aliquot $0.5 \pm 0.1\text{g}$.

Uptake sample by syringe, and weigh them (syringe + sample). Add in $3 \pm 1\text{ml}$ distilled water into an aluminum foil tray that its weight is known (W_1); inject sample by syringe and shake the aluminum foil tray so as to disperse sample in distilled water. In case that matters in the form of block appear, abandon the uptaken sample; and repeat the steps above to get a new one. And then weigh syringe, and reduced weight is the weight of sample that has been injected into the aluminum foil tray (S_a).

Keep the sample in $110 \pm 5^\circ\text{C}$ oven for 60min, then take out the sample, put it in a desiccator for cooling to room temperature, and then weigh it accurately to 0.1mg.

Calculate the percent weight:

$$V = 100 - (W_2 - W_1) \times 100 / S_a \quad (1)$$

Where: V — Percent weight of total volatile matter:

W_1 — Weight of aluminum foil tray, g ;

W_2 — Weight of dried aluminum foil tray + sample, g ;

S_a — Weight of aliquot sample, g.

The relative error of twice analytic results by a single analyzer should not be higher than 1.5%.

Part 2 Measuring method of moisture capacity in water soluble— gas chromatography

A.3 Instrument and reagent

A.3.1 Instrument

Gas chromatograph with thermal conductivity detector and temperature programming control;
Chromatographic column: column length 1.22m, outside diameter 3.2mm, load 60~80 mesh high molecular porous microsphere stainless steel column;

Recording instrument;

Microinjector: $1\mu\text{L}$ or $2\mu\text{L}$;

Glass container with stopper: 10ml.

A.3.2 Reagent

Anhydrous dimethyl formamide (DMF); chromatographically pure;

Anhydrous isopropyl alcohol.

A4 Measuring method

A.4.1 Instrumental operation condition

Vapourizing temperature of sample: 200°C;

Detector: temperature 240°C, electric current 150mA;

Column temperature: temperature programming, initial temperature 80°C, heating up rate 30°C/min, final temperature 170°C;

Carrier gas: >99.995% pure helium gas or high pure nitrogen.

A.4.2 Determination for response factor R of water

Weigh ~0.2g distilled water in the same glass container with stopper, and weigh ~0.2g isopropanol accurately to 0.1mg, add in 2ml dimethyl formamide, then mix completely. Inject 1 μl sample by microinjector, and record the chromatogram.

Calculate the response factor R of water:

$$R = \frac{W_i A_{H_2O}}{W_{H_2O} A_i} \quad (2)$$

Where: W_i —Weight of isopropanol, g;

W_{H_2O} —Weight of water, g;

A_{H_2O} —Peak area of water;

A_i —Peak area of isopropanol.

If isopropanol and dimethyl formamide are anhydrous reagents, use the sample quantity of isopropanol and dimethyl formamide (mixed liquor) as blank without adding in water; record the water peak area of the blank.

Calculate the response factor R of water:

$$R = \frac{W_i \times (A_{H_2O} - B)}{W_{H_2O} \times A_i} \quad (3)$$

Where: W_i —Weight of isopropanol, g;

W_{H_2O} —Weight of water, g;

A_i —Peak area of isopropanol.

A_{H_2O} —Peak area of water;

B—Water peak area of blank.

A.4.3 Sample analyses

Weigh 0.6g coating and 0.2g isopropanol accurately to 0.1mg, put them in glass container with stopper, then add in 2ml dimethyl formamide, close the stopper. Meanwhile, prepare a isopropanol and dimethyl formamide blank sample without adding coating. Shake sample vial vigorously for 15min, rest for 5min to deposit. Alternatively, use low speed centrifuge to deposit sample. Uptake 1 μl supernatant liquid in sample container, inject it into chromatographic column and record the chromatogram.

Calculate water content in coating by the equation below:

$$H_2O\% = \frac{A_{H_2O} \times W_i \times 100}{A_i \times W_C \times R} \quad (4)$$

Where: A_{H_2O} —Peak area of water;

A_i —Peak area of isopropanol.

W_i —Weight of isopropanol, g;

W_C —Weight of coating, g;

R—Response factor.

 Part 3 Calculation method for content of total volatile organic compounds (TVOC)

Calculate the content of total volatile organic compounds (TVOC) by the following equation:

$$TVOC = \frac{(V\% - H_2O\%) \times D_c}{100\% - H_2O\% (D_c / D_w)} \times 10^3 \quad (5)$$

Where: TVOC—— Content of volatile organic compounds in coating, g/L;

V ——Percent weight of volatile matter in coating;

H₂O% —— Percent weight of water in coating;

D_c —— Density of water soluble coating (determine according to GB 6750 - 86), g/ml;

D_w —— Water density, g/ml.

Annex B Determination for free formaldehyde in water soluble coating

B.1 Instrument and reagent

B.1.1 Instrument and equipment

Spectrophotometer, full glass still, measuring flask, 50ml Nessler tube, pipette, mortar.

B.1.2 Reagent

Unless described particularly in this standard, all reagents should be analytical reagent and distilled water or water with equivalent purity, all of which should accord with national standards or professional standards.

Sulfuric acid (H₂SO₄) : ρ = 1.84 g/ml.

Sodium hydroxide solution: c(NaOH) = 1mol/L.

Sulphuric acid solution: c (1/2H₂SO₄) = 1mol/L.

Sulphuric acid solution: c (1/2H₂SO₄) = 6mol/L.

Iodine solution: c (1/2I₂) ≈ 0.05 mol/L .

Acetylacetone solution: dissolve 50g ammonium acetate, 6ml glacial acetic acid and 0.5ml acetylacetone in 100ml water. This solution may be kept for at least one month in refrigerator.

Potassium dichromate standard solution: c(1/6 K₂Cr₂O₇) = 0.05 mol/L.

Sodium hyposulfite standard volumetric solution: c(Na₂S₂O₃ • 5 H₂O) ≈ 0.05 mol/L.

Formaldehyde(HCHO) standard solution:

Formaldehyde standard solution for usage:

Amylum indicator: 1 % (m/m).

B.2 Measurement procedure

B.2.1 Standard curve

Take several 50ml graduated tube with stoppers, add in 0.00, 0.50, 1.00, 3.00, 5.00, 8.00ml formaldehyde standard solution for usage, respectively; and add in water to 50ml. Heat for 30min in 60°C water bath, take out and cool it to room temperature, then determine it as soon as possible. Use 10mm color comparison container, select 414nm wavelength and measure absorbance; plot the standard curve of absorbance over corresponding formaldehyde amount.

B.2.2 Measurement for content of formaldehyde and calculation

Weigh 0.3 g sample (accurately to 0.001g), put it in a 100ml distillation flask which contain 20ml distilled water beforehand; heat and collect distillate. Make sure has add an amount of water in the flask to immerge export of condenser tube, and distil the sample to nearly dry. Transfer collected distillate in a 50mL graduated tube with stopper, dilute with water to scale and wait for measurement.

Add prepared sample in 2.5ml acetylacetone solution (3.6), and shake up. Heat for 30 in 60°C water bath, take out and cool it to room temperature, then determine it as soon as possible.

Use 10mm color comparison container, measure absorbance at 414nm wavelength; subtract

absorbance of measured from blank test and read the content of formaldehyde in the sample from the standard curve.

Substitute sample by 50ml water, conduct parallel operation.

B.2.3 Calculation for content of formaldehyde

Calculate formaldehyde content C (unit: mg/kg) according to the following equation:

$$C = \frac{m}{W} \quad (6)$$

Where: m ——Formaldehyde content looked up from standard curve, W—— Aliquot weighed, g.

Relative error between two measuring results should be less than 3%.

Annex C Determination for heavy metal in water soluble coating

Instrumentand equipment

C.1 Instrumentand equipment

C.1.1 Instrument

5 ml pipette with a big tummy;

100 ml tall glass beaker;

10.0 ml graduated pipette;

Electric hot plate;

100 ml measuring flask;

Flame atomic absorption spectrophotometer;

Pb, Cr, Cd hollow-cathode lamp;

C.1.2 Reagent

Nitric acid (GB626 - 78), 1% (V/V) nitric acid solution, perchloric acid(GB623-77), sulfuric acid(GB625 - 77), mixed acid: (nitric acid+perchloric acid+sulfuric acid =3 + 1 + 1), 1000 μ g/ml Cd standard solution, 1000 μ g/ml Cr standard solution, 1000 μ g/ml Pb standard solutoin, 50 μ g/ml Pb storage standard solution, 50 μ g/mlCd storage standard solution, 50 μ g/mlCr storage standard solution.

C.2 Measurement procedure

C.2.1 Preparation of test solution

Weigh ~1g sample accurately to 0.001g, and put it in tall glass beaker. Add 10ml mixed acid (3.2.5) in electric the beaker, then put it on electric hot plate to heat slowly. Gradually raise temperature after oxygenation of sample has completed, untill the volume of residual solution in beaker is less than 2ml. Cool it to room temperature and add in an amount of water. Then transfer it to 100ml measuring flask; filtration is needed if there are insoluble substances in the beaker. Blank sample should be prepared at the same time.

C.2.2 Measurement of lead content and calculation

C.2.2.1 Standard curve

Prepare the standard reference solution

Transfer lead storage standard solution by graduated pipette according to the volume listed in table 1 into 5 100 ml measuring flasks, then dilute it by nitric acid solution to scale, and shake up.

Table 1 Matching procedure for lead standard reference solution

Standard reference solution	Volume of pb storage standard solution /ml	Pb standard solution / μ g/ml
Blank	0	0
1	2.0	1.0
2	4.0	2.0
3	8.0	4.0
4	10.0	5.0

Attach lead hollow-cathode lamp to spectrograph, tune wavelength at 217.0nm; regulate

instrument to optimum condition of measuring lead according to instruction . Adjust flow of acetylene and air; light up flame; optimize the measurement of absorbency for standard reference solution.

Draw each standard reference solution (5.1.1) to flame by the order of from low concentration to high concentration, and read out the absorbency.

Standard curve

Plot a curve as x axis is the lead concentrations of standard reference solution (in $\mu\text{g/ml}$) and y axis is the difference values between corresponding absorbencies of solution and absorbencies of blank solution.

Draw test solution into flame, and read out the absorbency. If absorbency of test solution is higher than that of maximum lead standard reference solution, this test solution should be diluted by nitric acid solution (3.2.2) (with dilution factor F).

C2.2.2 Calculation

Lead percentage of water soluble coating (the result round to 1-digit).

$$Pb\% = \frac{C - C_0}{S} \times V \times F \times 10^{-4} \quad (7)$$

Where: C_0 —Lead concentration on blank test solution, $\mu\text{g/ml}$;

C — Lead concentration of test solution looked up from standard curve, $\mu\text{g/ml}$;

F — Dilution factor;

S — Sample mass, g;

V — Volume of sample solution, ml.

C2.3 Measurement for content of Cd and calculation

C2.3.1 Standard curve

Prepare the standard reference solution

Transfer Cd storage standard solution by graduated pipette according to the volume listed in table 2 into five 100 ml measuring flasks, then dilute it by nitric acid solution to scale, and shake up.

Table 2 Preparing procedure of Cd standard reference solution

Standard reference solution	Volume of Cd storage standard solution /ml	Cd standard solution / $\mu\text{g/ml}$
0	0	0
1	1.0	0.5
2	2.0	1.0
3	3.0	1.5
4	4.0	2.0

Attach Cd hollow-cathode lamp to spectrograph, tune wavelength at 228.8nm; regulate instrument to optimum condition of measuring Cd according to instruction . Adjust flow of acetylene and air; light up flame; optimize the measurement of absorbency for standard reference solution. Draw each standard reference solution to flame by the order of from low concentration to high concentration, and read out the absorbency.

Standard curve

Plot the curve as x axis is concentration of Cd standard reference solution, and y axis is the difference values between the corresponding absorbency and blank solution absorbency.

Draw test solution into flame, and read out the absorbency. If absorbency of test solution is higher than that of maximum Cd standard reference solution, this test solution should be diluted by nitric acid solution (with dilution factor F) .

C2.3.2 Calculation

Cd percentage of water soluble coating (the result round to 1-digit).

$$Cd\% = \frac{C - C_0}{S} \times V \times F \times 10^{-4} \quad (8)$$

Where: C_0 —Cd concentration of blank test solution, $\mu\text{g/ml}$;

C — Cd concentration of test solution read from standard curve, $\mu\text{g/ml}$;

F — Dilution factor;

S — Sample mass, g;

V — Volume of sample solution, ml.

C2.4 Measurement for content of Cr and calculation

C2.4.1 Standard curve

Prepare the standard reference solution

Transfer Cr storage standard solution by graduated pipette according to the volume listed in table 3 into five 100 ml measuring flasks, then dilute it by nitric acid solution to the scale, and shake up.

Table 3 Preparing Cr standard reference solution

Standard reference solution	Volume of Cr storage standard solution /ml	Cr standard solution / μ g/ml
0	0	0
1	1.0	0.5
2	2.0	1.0
3	3.0	1.5
4	4.0	2.0

Attach Cr hollow-cathode lamp to spectrograph, tune wavelength at 357.9nm; regulate instrument to optimum condition of measuring Cr according to instruction. Adjust flow of acetylene and air; light up flame; optimize the measurement of absorbency for standard reference solution. Draw each standard reference solution to flame by the order of from low concentration to high concentration, and read out the absorbency.

Standard curve

Plot the curve as x axis is concentration of Cr standard reference solution, and y axis is the difference values between the corresponding absorbency and blank solution absorbency.

Draw test solution into flame, and read out the absorbency. If absorbency of test solution is higher than that of maximum Cr standard reference solution, this test solution should be diluted by nitric acid solution (with dilution factor F).

C.2.4.2 Calculation

Cr percentage of water soluble coating (the result round to 1-digit).

$$Cr\% = \frac{C - C_0}{S} \times V \times F \times 10^{-4} \quad (9)$$

Where: C_0 — Cr concentration of blank test solution, μ g/ml;

C — Cr concentration of test solution looked up from standard curve, μ g/ml;

F — Dilution factor;

S — Sample mass, g;

V — Volume of sample solution, ml.

C2.5 Measurement for content of mercury and calculation

C.2.5.1 Measurement

See also "Paints and varnishes--Determination of "soluble" metal content--Part 7: Determination of mercury content of the pigment portion of the paint and of the liquid portion of water-dilutable paints--Flameless atomic absorption spectrometric method" (GB 9758.7-88).

C.2.5.2 Calculation

Hg percentage of water soluble coating (the result round to 1-digit).

$$Hg\% = \frac{C - C_0}{S} \times V \times F \times 10^{-4} \quad (10)$$

Where: C_0 — Hg concentration of blank test solution, μ g/ml;

C — Hg concentration of test solution read from standard curve, μ g/ml;

F — Dilution factor;

S — Sample mass, g;

V — Volume of sample solution, ml.

Annex D Determination for halon, benzene, toluene, xylene in water soluble coating

D.1 Instrument and reagent

D.1.1 Instrument

Carrier gas: high purity nitrogen

Combustion gas: hydrogen gas, degree of purity >99.8%

Combustion-supporting gas: air

Gas chromatograph: any chromatograph with hydrogen flame ionization detector that could meet the the analysis condition 6; benzene detection limit $D \leq 1 \times 10 \times 10^{-9} \text{g/s}$

Chromatographic column: nonpolarity adsorption capillary column, 0.25 mm x 30 m x 25 μ m (membrane thickness) (Such as HP -1, DB -1)

Sample injector: head-space sampling device which could meet the analysis condition.

Head-space sample bottle: 20ml

Disposable syringe, 5ml

D.1.2 Reagent

Dichloromethane, analytically pure

1.1 - Dichloroethane, analytically pure

1.2 - Dichloroethane, analytically pure

1.1.1 - trichloroethane, analytically pure

1.1.2 - trichloroethane, analytically pure

Carbon tetrachloride, analytically pure

Benzene, analytically pure

Toluene, analytically pure

Xylene (mixture of m-, o-, p- xylene), analytically pure

Methanol, analytically pure

D.2 Testing procedure

D.2.1 Chromatographic operation condition

Head-space sample injector

Temperature of water bath: 50 °C

Equilibration period: 60min

Volume of quantified tube: 10 μ l, Temperature 85 °C

Temperature of gas transfer lines: 85 °C

Gas chromatograph condition

Sample mode: split stream sampling

Split ratio: 80 : 1 (20:1 if it is without head-space sample injector; 80:1 if it is with head-space sample injector)

Velocity of carrier gas flow: 1.0ml/min

Hydrogen flow rate: 30ml/min

Air-flow rate: 380ml/min

Column temperature: temperature programming, 40°C, keep for 4 min; then raise temperature to 150°C at 10°C/min, and keep for 5 min.

Injection port temperature: 150°C

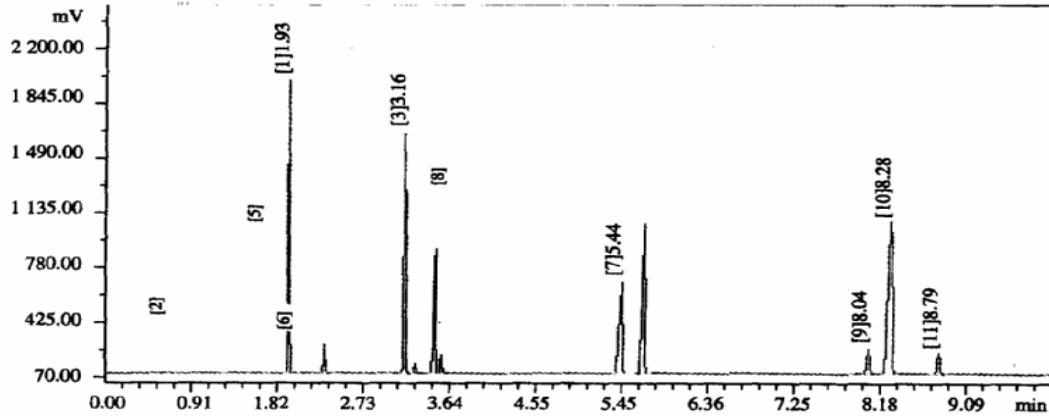
Detector temperature: 250°C

Make-up gas: 10ml/min

Chromatographic column aging: age overnight (about 16h) at 280°C

D.2.2 Measurement procedure

Determination for retention time of substances being measured: add standard substance being measured in sample bottle (6.4); put it in head-space sample injector; automatically sample into chromatograph by head-space sample injector after the instrument being stable in the given chromatographic condition; record the retention time of each component. Retention time of each component is as follows:



Peak 1- methanol, peak 2 - dichloromethane, peak 3 - 1.2 - Dichloroethane, peak 4 - 1.1.1 - trichloroethane, peak 5 - benzene, peak 6 - carbon tetrachloride, peak 7 - toluene, peak 8 - 1.1.2 - trichloroethane, peak 9- P-xylene, peak 10 - m-xylene, peak 11 - o-xylene

Quantify components in the sample: put 2 g sample in the sample bottle; measure it according to 8.1; determine contained substances according to the chromatogram. If contained substances are determined, record their peak area.

Preparing mixed standard solution: prepare mixed standard solution by using methanol (5.10) as solvent according to substances determined in 8.2. As for amount of component in the mixed standard solution, prepare them according to the following requirement: a. the amount should be ~10% of the taken sample amount; b. peak area of each standard component in the mixed standard solution should be less than the peak area of that in sample. Sample measurement: Take sample by syringe (6.5) (the sample should be fully homogeneous, do not permit stir the sample by stirring rod); weigh 2 g sample by taking sample out, with accuracy of 0.0002g; Inject into two sample bottles, respectively; then weigh standard solution(8.3) accurately by taking solution out; inject into one of the two sample bottles; and determine the weighed mixed standard solution according to 8.2, and seal sample bottle as soon as possible.

Put the weighed sample bottle into head-space sample injector. Test it after the instrument get stable, and calculate the testing result.

Calculation: Calculate concentration, C_x , of each substance according to equation 12:

$$C_x = \frac{A_{S2} \times W_{std} \times C_{std}}{A_{S1+Std} \times W_{S2} - A_{S2} \times W_{S1}} \times \frac{1}{R} \times 100 \quad (12)$$

Where, A_{S1+Std} —Peak area in chromatogram of sample 1 which has added in standard solution;

A_{S2} — Peak area in chromatogram of sample 2;

C_x —Percent of tested substance;

C_{std} — Concentrations of standard components in mixed standard solution, %;

W_{S1} — Mass of sample 1, g;

W_{S2} —Mass of sample 2, g;

W_{std} —Amount of mixed standard solution added in sample 1, g.

$$R = \frac{\rho_{水} - \rho_{样} \times L}{\rho_{水} \times \rho_{样}} \quad (13)$$

Where, L —Percent of water in water soluble coating;

$\rho_{样}$ —Determine the density of coating according to GB675-86, g/ml

$\rho_{水}$ —Water density, 25 °C , g/ml.

Result of calculation should round to 3-digit significant figures.