50～64	12	255～296	20
65～81	13	297～343	21
82～101	14	344～394	22
102～125	15	395～450	23
126～151	16	451～512	24
152～181	17		

6.4.2 Bulk products

Implement as specified in GB/T 6679.

6.5 Sample reduction and preparation

6.5.1 Sample reduction

Mix the sample quickly and divide the sample to about 1 kg with a divider or quartering method. Then divide it into two parts and put them in two clean, dry 500 mL glass bottles with grinding plugs or plastic bottles (The quality inspection department of the production enterprise can use clean and dry plastic self-sealing bags to hold samples). Sealed and labeled, indicating the name of the manufacturer, product name, batch number or production date, sampling date and name of the sampler. One bottle is used for product quality analysis, and the other bottle should be kept for 2 months for future reference.

6.5.2 Sample preparation

Take a bottle of sample (6.5.1), take out about 100 g of sample after reduction, air dry, grind to pass the 0.2 mm pore size test sieve, mix well, and place in a clean and dry bottle for component analysis. The remaining samples are used for particle size determination.

6.6 Judgment of qualified quality specifications

Adopt the "rounding off value comparison method" in GB/T 8170 to judge the qualification of the quality specification.

7 Marking

7.1 The front of the products' packaging container shall be marked with the name of the production or business enterprise, the name of the product, the standard number, the production date, and indicate the total content of humic acid and fulvic acid, cation exchange capacity, total nitrogen content, nitrate nitrogen content and net content.

7.2 The net content of each bag shall be marked with a single value, such as 40 kg, 25 kg or 10 kg. The other requirements shall comply with GB 18382.

8 Packaging, transport and storage

8.1 Carry out the package of the products as specified in GB/T 8569. The packaging specification is 40 kg, 25 kg or 10 kg, and for each bag, the allowed range of the net content is (40±0.4) kg, (25±0.25) kg and (10±0.1) kg respectively. For each batch of products, the average net content of each bag has not be less than 40.0 kg, 25.0 kg and 10.0 kg. When users have special requirements for the net content of each bag, it can be negotiated by both parties and take the contract for criterion.

8.2 The products shall be stored in a flat, cool and dry place, and during transport, the products shall be moisture-proof, sun-proof and crack-proof, and the warning instructions are implemented according to those specified in GB/T 191.

Annex A

(Normative)

Determination of total amount of humic acid and fulvic acid—Residue method

A.1 Method summary

The sample was extracted with 1% sodium hydroxide, the insoluble matter was centrifuged, filtered, washed and dried, and then corrected with the burning residue. Finally, the mass fraction of organic matter was calculated as the total content of humic acid and fulvic acid.

A.2 Reagents

Sodium hydroxide solution，ω（NaOH）= 1 %.

Weigh 10 g of analytical pure sodium hydroxide (NaOH), put it into a beaker, dissolve with distilled water, cool, and add water to 1 L.

A.3 Apparatuses

A.3.1 Analytical balance: sensitivity 0.000 1 g.

A.3.2 Thermostat water bath: control accuracy (100±2) ℃.

A.3.3 Constant temperature drying box: the temperature can be controlled at (110±5) ℃.

A.3.4 Centrifuge: Minimum speed 2 000 r/min, the volume of centrifugal cup is more than 400 mL.

A.3.5 Muffle furnace: control accuracy (815±10)℃.

A.3.6 Quantitative filter paper: diameter 18 cm.

A.3.7 Weighing bottle with grinding plug: diameter 50 mm, height 30 mm.

A.3.8 Porcelain crucible: 50 mL.

A.4 Test procedures

A.4.1 Dissolution

Weigh 0.5 g～1.0 g (m,accurate to 0.000 2 g) of the analytical sample into a 250 mL triangular flask, add 100 mL sodium hydroxide solution, shake to make the sample wet, cover a small funnel at the mouth of the conical flask, place it in a boiling water bath, heat and extract for 2 h, shake once every 20 min to make the sample evenly extracted. At the same time, do the blank experiment, washing times and washing water should be

consistent as far as possible.

A.4.2 Centrifugation, filtration

Take out the conical flask, cool it to room temperature, centrifuge the extract at the speed of (3 000～3 500) r/min for 30 min, and transfer the centrifuged clear liquid to the slow quantitative filter paper which has already been dried at 105 ℃～110 ℃ to constant weight. Add 50 mL water to the centrifugation residue, stirred well, and centrifuged at (3 000-3 500) r/min for 30 min. Wash the residue three times according to the above washing steps and avoid penetrate. Finally, transfer the residue to the filter paper and washed with water till neutral.

A.4.3 Drying, constant weight

Transfer the precipitate and filter paper to the weighing bottle and put in the 105 ℃～110 ℃ drying oven for 2 h. Take it out, cool down in air for 2～3 min, then put it into a dryer to cool down to room temperature (about 20 min), and weigh it. Carry out inspection drying until the difference between the two consecutive times is not more than 0.001 g, calculate the mass (m_3), and weigh the blank mass (m_1).

A.4.4 Burning

Transfer the dried and constant weight precipitate in A.4.3 together with filter paper into the round bottom porcelain crucible (A.3.8) which has been constant weighted, put it in the muffle furnace with a gap of 15 mm～20 mm left in the furnace door. Rising temperature to 250 ℃～300 ℃, Slow ashing, then close the furnace door and burn at (815 ± 10)℃ for 1 h. Take out the crucible from muffle furnace, cool it in air for 5 min, then put it into dryer, cool it to room temperature (about 20 min), and weigh it. Conduct inspection burning until the difference between two consecutive times is not more than 0.001 g, and calculate the mass of burning residue of sediment (m_4) and blank burning residue (m_2).

A.4.5 Determination of ash content

Implement as specified in GB/T 212.

A.5 Expression of analysis results

The value of mass fraction $(HA+FA)_d$ of humic acid and fulvic acid content (dry basis) is expressed as %, calculated according to formula (A.1):

$$(HA+FA)_d = \frac{\frac{m-(m_3-m_4)-(m_1-m_2)}{m}\times 100 - M_{ad} - A_{ad}}{1-(M_{ad}/100)} \times 100\% \quad \text{(A.1)}$$

Where

m is the value of sample, in grams (g);
m_3 is the value of precipitate after drying, in grams (g);
m_4 is the value of sediment burning residue, in grams (g);
m_1 is the value of blank filter paper after drying, in grams (g);
m_2 is the mass of burning residue of blank filter paper, in grams (g);
M_{ad} is the moisture of the sample, expressed as % ;
A_{ad} is ash of the sample, expressed as % .

Take the arithmetic mean of the parallel measurement results as the measurement results, and the results is reserved to one decimal place.

A.6 Allowable deviation

The results of parallel determination and the relative difference between the results of different laboratories shall comply with the requirements in Table A.1.

Table A.1 — Allowable deviation of determination results of humic acid and fulvic acid

$(HA+FA)_d$ /%	Same lab *d* /%	Different labs *d* /%
＜40	1.0	1.5
≥40	1.5	2.0

Annex B

(Normative)

Determination of cation exchange capacity (C.E.C.) Hydrochloric acid back dropping method

B.1 Method summary

The acidic functional groups in humic acid molecules, especially carboxyl groups, have large exchange capacity and fast exchange rate. Therefore, the acidic functional groups are the main factor for the exchange capacity of humic acid. The reaction between nitric acid and humic acid greatly increases the oxygen-containing functional groups of humic acid. The determination of the exchange capacity of humic acid and fulvic acid is to detect the exchange capacity of acidic functional groups. Therefore, the method of direct reaction of sodium hydroxide with hydrochloric acid is the most suitable.

The sample fully reacts with the excess sodium hydroxide solution, and then titrates the excess sodium hydroxide with standard hydrochloric acid solution. The titration end point is pH = 8.4. The cation exchange capacity (C.E.C.) of the sample is calculated according to the difference between alkali and acid consumption.

B.2 Reagents

B.2.1 Ethanol: chemically pure.

B.2.2 Sodium hydroxide: analytical pure.

B.2.3 Phenolphthalein: analytical pure.

B.2.4 Phenolphthalein indicator: ρ（$C_{20}H_{14}O_4$）= 10 g/L.

Weigh 1.0 g of analytically pure phenolphthalein (B.2.3), dissolve in ethanol, and dilute with ethanol to 100 mL.

B.2.5 Sodium hydroxide standard solution: c（NaOH）= 0.1 mol/L.

Weigh 4.0 g of analytically pure sodium hydroxide (B.2.2) and dissolve it in 1000 mL of boiled carbon dioxide free distilled water.

Calibration method: Grind 10 g～20 g of reference potassium hydrogen phthalate ($KHC_8H_4O_4$) into powder with agate mortar, dry it in a 120 ℃ drying oven for 2 h, and cool it in a dryer.

Accurately weigh about 0.90 g～1.00 g (accurate to 0.000 1 g) of dried reference potassium hydrogen phthalate, place it into a 250 mL conical flask, add 100 mL distilled water without carbon dioxide, shake it to completely dissolve, add 2 drops of phenolphthalein indicator solution (B.2.4), and drip the solution to be calibrated to make the solution from colorless to light red as the end point. Blank determination was performed at the same time.

The concentration c (NaOH) of sodium hydroxide standard solution is expressed as mol/L and calculated according to formula (B.1):

$$c(NaOH)=\frac{m}{(V_1-V_2)\times 0.2042} \quad \text{(B.1)}$$

Where

m is the value of potassium hydrogen phthalate, in grams (g);

V_1 is the value of volume of sodium hydroxide standard solution consumed during titration, in milliliters (mL);

V_2 is the value of volume of sodium hydroxide standard solution consumed in blank, in milliliters (mL);

0.204 2 is the value of potassium hydrogen phthalate in grams equivalent to 1.00 mL sodium hydroxide standard solution c (NaOH) = 1.000 mol/L, in grams per millimole (g/mmol).

B. 2. 6 Hydrochloric acid: analytical purity.

B. 2. 7 Anhydrous sodium carbonate: analytical purity.

B. 2. 8 Methyl Orange: analytical pure.

B. 2. 9 Methyl red indicator solution: 1 g/L.

Weigh 0.10 g of methyl red, dissolve in ethanol, and dilute with ethanol to 100 mL.

B. 2. 10 Hydrochloric acid standard solution: c (HCl) = 0.1 mol/L.

Take 8.3 mL of analytical pure hydrochloric acid with relative density of 1.19, dilute with water to 1000 mL, shake well and calibrate.

Calibration method: accurately weigh 0.22 g (accurate to 0.001 g) of reference anhydrous sodium carbonate dried at 250 ℃ for 4 hours, put it into a 250 mL conical flask, add 50 mL of water to dissolve it, add 2 drops of methyl red indicator solution, titrate with hydrochloric acid solution till the red just appears, carefully boil the solution till the red fades, cool to room temperature, and continue titration, boiling and cooling, Until the emerging reddish color does not fade when reheated. Blank determination was performed at the same time.

The concentration c (HCl) of hydrochloric acid standard solution is expressed as mol/L and calculated

according to formula (B.2):

$$c(HCl) = \frac{m}{(V_3 - V_4) \times 0.05299} \quad \text{(B.2)}$$

Where

m——is the value of anhydrous sodium carbonate, in grams (g);

V_3——is the value of volume of hydrochloric acid standard solution consumed in titration of anhydrous sodium carbonate, in milliliters (mL);

V_4——is the value of volume of hydrochloric acid standard solution consumed when titrating blank, in milliliters (mL);

0.052 99——is the mass of anhydrous sodium carbonate in grams equivalent to 1.00 mL hydrochloric acid standard solution c (HCl) = 1.000 mol/L, in grams per millimole (g/mmol).

B.3 Apparatuses

B.3.1 Analytical balance: sensitivity 0.000 1 g.

B.3.2 Automatic potentiometric titrator: the resolution is 0.01 pH, and the determination range is 0 pH～14 pH.

B.4 Analysis procedures

Accurately weigh 0.5 g (accurate to 0.000 2 g) of the analytical sample into a 100 mL beaker, add a few drops of ethanol to wet the sample, then add 10 mL distilled water, place the beaker on the automatic potentiometric titrator, add 25 mL 0.1 mol/L sodium hydroxide standard solution (B.2.5) with a pipette under electromagnetic stirring to fully dissolve it (about 1 h), The excess sodium hydroxide is back-dropped with 0.1 mol/L hydrochloric acid standard solution (B.2.10), the end point is pH = 8.4, the dosage of sodium hydroxide standard solution (V_5) and the consumption of hydrochloric acid standard solution (V_6) are recorded, and then calculate the cation exchange capacity of the sample. Blank determination was performed at the same time.

B.5 Expression of analysis results

The value of cation exchange capacity $[C.E.C.]_d$ (on dry basis) is expressed as cmol/kg, calculated according to formula (B.3):

$$[C.E.C.]_d = \frac{[c(HCl) \times (V_0 - V_6)] \times 10 \times 1000}{m \times (100 - M_{ad})} \quad \text{(B.3)}$$

Where

c（HCl）—— is the concentration of hydrochloric acid standard solution, in moles per liter (mol/L);

V_0 —— is the volume of hydrochloric acid standard solution consumed during blank titration, in milliliters (mL);

V_6 —— is the volume of hydrochloric acid standard solution consumed when titrating the sample, in milliliters (mL);

10 —— is the multiple when convert mmol to cmoL;

1000 —— is the converted to cmoL per kilogram;

m —— is the value of the sample, in grams (g);

M_{ad} —— is the moisture of the sample,expressed as %.

Take the arithmetic mean of the parallel measurement results as the measurement results, and the results is reserved to one decimal place.

B.6 Allowable deviation

The results of parallel determination and the relative difference between the results of different laboratories shall comply with the requirements in Table B.1.

Table B.1 — Allowable deviation of cation exchange capacity (C.E.C.) measurement results

Same lab d /(cmol/kg)	Different labs d /(cmol/kg)
15	25

Annex C

(Normative)

Determination of nitrate nitrogen content Dewada alloy reduction distillation titration

C.1 Method summary

The nitrate nitrogen in the sample is reduced to ammonia by devada alloy, distilled with alkali, and absorbed by boric acid. Titrate with hydrochloric acid standard solution, calculate the content of available nitrogen according to the consumption of hydrochloric acid standard solution, and determine and deduct the content of ammonium nitrogen, so as to obtain the nitrate nitrogen content in the sample.

C.2 Reagents

C.2.1 Devada alloy (copper aluminum zinc alloy, mass ratio 50:5:45): analytical pure.

C.2.2 Sodium hydroxide solution, ρ（NaOH）= 400 g/L.

Weigh 400 g of analytically pure sodium hydroxide, dissolve it in boiled distilled water without CO_2, and fix the volume to 1 L.

C.2.3 Sodium hydroxide solution, ρ（NaOH）= 4 g/L.

Weigh 4 g of analytically pure sodium hydroxide, dissolve it in boiled distilled water without CO_2, and fix the volume to 1 L.

C.2.4 Boric acid solution, ρ（H_3BO_4）=20 g/L.

Weigh 20 g boric acid, dissolve it in a little amount of water, dilute it to 1 L, heat it to dissolve, filter out the insoluble matter and store it.

C.2.5 Hydrochloric acid standard solution, c（HCl）=0.1 mol/L.

Complying with B.2.10 in Annex B.

C.2.6 Bromocresol green indicator solution, ρ（$C_{21}H_{14}Br_4O_5S$）= 1 g/L.

Weigh 0.10 g of analytically pure bromocresol green, dissolve in 6 mL of sodium hydroxide solution (4 g/L) and 5 mL of ethanol, dilute with water to 100 mL, and shake well.

C.2.7 Methyl red indicator solution, ρ（$C_{15}H_{15}N_3O_2$）= 1 g/L.

Weigh 0.10 g of analytically pure methyl red, dissolve in ethanol, dilute with ethanol to 100 mL, and shake well.

C.2.8 Bromocresol green methyl red mixed indicator.

Mix 3 parts by volume of bromocresol green indicator solution (1 g/L) and 1 part by volume of methyl red indicator solution (1 g/L), shake well and store in a brown bottle.

C.3 Apparatuses

C.3.1 General laboratory instruments.

C.3.2 Nitrogen determination distiller or distillation unit.

C.4 Test procedures

Accurately weigh 0.5 g (m, accurate to 0.000 2 g) of analytical sample into a 1 000 mL long neck distillation flask, add 400 mL distilled water, 1 g devada alloy and a little paraffin, add 40 mL of 20 g/L boric acid solution (C.2.4) and 3 drops of bromocresol green methyl red mixed indicator (C.2.8) into the absorption flask, smear the interface of nitrogen determination distiller with silicone grease, and install the distillation device, Add 10 mL of 400 g/L sodium hydroxide solution (C.2.2) into the bypass pipe above the distillation flask, wash the pipeline with a little water and seal it with water, and start distillation after violent reaction for 5 min; Distill until the volume of the absorption solution reaches 150 mL, remove the absorption bottle, titrate the solution with 0.1 mol/L hydrochloric acid standard solution (C.2.5), change the solution from green to wine red, that is, reach the titration end point, and calculate the nitrate nitrogen content according to the consumption of hydrochloric acid standard solution (V_7). At the same time, conduct blank determination, and record the volume of hydrochloric acid standard solution consumed by blank (V_8).

C.5 Determination of ammonium nitrogen content

Measure the ammonium nitrogen content of the sample, the determination method preformed as specified in Annex A of HG/T 3276-2019.

C.6 Expression of analysis results

The value of the mass fraction of nitrate nitrogen content $(NO_3^-\text{-}N)_d$(on dry basis) expressed as %, and is calculated according to formula (C.1):

$$(NO_3 - N)_d = \frac{c(HCl) \times (V_7 - V_8) \times 0.014 \times 100}{m \times (100 - M_{ad})} - \frac{(NH_4^+ - N)_{ad} \times 100}{100 - M_{ad}} \quad \text{(C.1)}$$

Where

c（HCl） is the value of the concentration of hydrochloric acid standard solution, in moles per liter (mol/L);

V_7 is the value of the volume of hydrochloric acid standard solution consumed when titrating the sample, in milliliters (mL);

V_8 is the value of the volume of hydrochloric acid standard solution consumed when titrating blank, in milliliters (mL);

0.014 is the value of millimolar mass of nitrogen, in grams per millimole (g/mmol);

m is the value of the mass of sample, in grams (g);

M_{ad} is the moisture of the sample, expressed as %.

Take the arithmetic mean of the parallel measurement results as the measurement results, and the results is reserved to one decimal place.

C.7 Allowable deviation

The results of parallel determination and the relative difference between the results of different laboratories shall comply with the requirements in Table C.1.

Table C.1 — Allowable deviation of nitrate nitrogen content determination results

Same lab *d*/%	Different labs *d*/%
0.1	0.2

Annex D

(Normative)

Determination of free nitric acid content
Sodium hydroxide direct titration (rapid method)

D.1 Method summary

The free nitric acid in the sample is dissolved, constant volume and filtered with water. The filtrate is titrated with sodium hydroxide standard solution. The content of free nitric acid in the sample is calculated according to the amount of sodium hydroxide standard solution consumed when titrated to pH = 7.

D.2 Reagents

D.2.1 Ethanol: chemically pure.

D.2.2 Sodium hydroxide: analytical pure.

D.2.3 Phenolphthalein: analytical pure.

D.2.4 Phenolphthalein indicator solution, ρ（$C_{20}H_{14}O_4$）= 10 g/L.

Weigh 1.0 g phenolphthalein (B.2.3), dissolve in ethanol, and dilute with ethanol to 100 mL.

D.2.5 Sodium hydroxide standard solution, c（NaOH）= 0.1 mol/L.

Implement as specified in B.2.5 of Annex B.

D.3 Apparatuses

D.3.1 Analytical balance: sensitivity 0.000 1 g.

D.3.2 Automatic potentiometric titrator: the resolution is 0.01 pH, and the measurement range is 0 pH～14 pH.

D.3.3 Horizontal reciprocating oscillator: amplitude 20 mm, stepless speed regulation 0 times/min～300 times/min.

D.4 Test procedures

Accurately weigh 5 g (m, accurate to 0.000 2 g) of analytical sample into a 300 mL triangular flask, add 100 mL distilled water and shake well. Place it on a horizontal reciprocating oscillator and vibrate for 30 min to dissolve free nitric acid in water. Transfer the oscillating solution to a 200 mL volumetric flask with water, fix the volume, shake well for use.

Filter with medium speed qualitative filter paper, discard the initial 10 mL filtrate, accurately suck 50 mL

filtrate, place it in a 250 mL beaker, place the beaker on the automatic potentiometric titrator, drip 0.1 mol/L sodium hydroxide standard solution (D.2.5) under electromagnetic stirring to pH = 7 as the end point, and record the consumption of sodium hydroxide standard solution (V_9). At the same time, conduct blank determination and record the volume of sodium hydroxide standard solution consumed in blank (V_{10}).

D.5 Expression of analysis results

The value of the mass fraction of free nitric acid content ($HNO_{3,d}$) (on dry basis) expressed as %, is calculated according to formula (D.1):

$$HNO_{3,d} = \frac{c(NaOH) \times (V_9 - V_{10}) \times 0.06301 \times 100}{(m \times 50 / 200) \times (100 - M_{ad})} \times 100 \cdots\cdots\cdots\cdots\cdots\cdots (D.1)$$

Where

c(NaOH)—is the value of the concentration of sodium hydroxide standard solution, in moles per liter (mol/L);

V_9 —is the value of the volume of sodium hydroxide standard solution consumed when titrating the sample, in milliliters (mL);

V_{10} —is the value of the volume of sodium hydroxide standard solution consumed when titrating blank, in milliliters (mL);

0.063 01—is the value of the millimolar mass of nitric acid, in grams per millimole (g/mmol);

m —is the value of the mass of the sample, in grams (g);

50 —is the value of the volume of solution to be titrated, in milliliters (mL);

200—is the value of the total volume of solution to be titrated, in milliliters (mL);

M_{ad}—is the moisture of the sample, expressed as %.

Take the arithmetic mean of the parallel measurement results as the measurement results, and the results is reserved to one decimal place.

D.6 Allowable deviation

The results of parallel determination and the relative difference between the results of different laboratories shall comply with the requirements in Table D.1.

Table D.1 — Allowable deviation of determination results of free nitric acid content

Same lab d /%	Different labs d /%
0.1	0.2

Annex E

(Normative)

Determination of free nitric acid content
Determination of nitrogen by water-soluble filtrate (arbitration method)

E.1 Method summary

The free nitric acid in the sample is dissolved, constant volume and filtered. The filtrate is determined by dewadar alloy reduction distillation. The content of free nitric acid in the sample is calculated according to the content of nitrate nitrogen in the filtrate.

E.2 Reagents

Same as Annex C.

E.3 Apparatuses

E.3.1 Analytical balance: sensitivity 0.000 1 g.

E.3.2 Horizontal reciprocating oscillator: amplitude 20 mm, stepless speed regulation 0 times/min～300 times/min.

E.3.3 Nitrogen determination unit or distillation unit.

E.4 Test procedures

Accurately weigh 5 g (m, accurate to 0.000 2 g) of the analytical sample into a 300 mL conical flask, add 100 mL of distilled water, shake well, place it on a horizontal reciprocating oscillator and shake for 30 min to dissolve free nitric acid in water. Transfer the oscillating solution to a 200 mL volumetric flask, constant volume, shake well for use.

Filter with medium speed qualitative filter paper, discard the initial 10 mL filtrate, accurately suck 50 mL filtrate, put it into a 1 000 mL long neck flask, and operate according to the steps in Annex C.4 to obtain the nitrate nitrogen content in the filtrate. Meanwhile, the ammonium nitrogen content in the filtrate shall be determined according to the provisions in Annex A of HG/T 3276—2019.

E.5 Expression of analysis results

The value of the mass fraction of free nitric acid content ($HNO_{3,d}$) expressed as %, is calculated according to formula (E.1):

$$HNO_{3,d} = \frac{(NO_3^- - N)_d \times 0.06301}{0.014} \quad \text{(E.1)}$$

Where

$(NO_3^-\text{-}N)_d$ —is the nitrate nitrogen content in the filtrate according to the method in Annex C, expressed as %;

0.063 01—is the value of millimolar mass of nitric acid, in grams per millimole (g/mmol);

0.014—is the value of millimolar mass of nitrogen, in grams per millimole (g/mmol).

Take the arithmetic mean of the parallel measurement results as the measurement results, and the results is reserved to one decimal place.

E.6 Allowable deviation

The results of parallel determination and the relative difference between the results of different laboratories shall comply with the requirements in Table E.1.

Table E.1 — Allowable deviation of determination results of free nitric acid content

Same lab *d* /%	Different labs *d* /%
0.1	0.2