RESOLUTION OENO 11/2003

BENTONITES

THE GENERAL ASSEMBLY,

CONSIDERING Article 5 of the International Convention on the Unification of the Methods of Analysis and Appraisal of Wines of 13 October 1954,

UPON THE PROPOSAL of the Sub Commission on Methods of Analysis and Appraisal of Wines,

DECIDES to replace the existing monograph by the following monograph in the International Oenology Codex:

BENTONITES

Bentonita

N° SIN: 558

1. OBJECT, ORIGIN AND FIELD OF APPLICATION

Bentonites are hydrous aluminium silicates belonging to the montmorillonite group. The brute formula is:

$$Si_4\left(Al_{(2-x)}\,R_X\right)(O_{10},H_2O)\,(Ce_x,nH_2O)\;or\;Si_4\left(Al_{(2-x)}\,R_x\right)(H_2O)n\;where:$$

$$R = Mg, Fe, M, Zn, Ni$$

$$Ce\;(exchangeable\;cations) = Ca, Na, Mg$$

Bentonites are used for clarification operations or protein stabilisation in musts and wine. Bentonites fix to certain unstable proteins which allows them to be eliminated.

Bentonites are capable of fixing coloured matter.

2. LABELLING

The nature of the bentonite (natural sodium, calcium, and activated calcium), batch number and the optimal expiration date for activated bentonites will be indicated on

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003

the label. The mention of risks and safety concerning the presence of crystalline silica should also be indicated.

2.1. Natural Bentonites:

Depending on the nature of the of exchangeable cations present, there are 2 naturally occurring types of bentonite:

- Sodium bentonite, it swells and absorbs readily where sodium is the major exchangeable cation.
- Calcium bentonite, where calcium is the major exchangeable cation, it is lower swelling and lower absorbent than sodium bentonites.

These two types of betonites are simply grinded before their commercialisation after possibly being dried at 80°C to 90°C.

2.2. Activated bentonites:

In order to improve the adsorption properties of calcium betonites, they are most often activated by sodium carbonate, then dried and grinded. This results in activated calcium bentonites with properties equal or superior to sodium bentonites.

The properties of these bentonites thus activated or permuted are less stable in time (3 to 18 months) and depend on the activation of magnesium, calcium, and sodium levels.

These different types of bentonites are in the form of powder, spherical or cylindrical granules. Colour can vary from white for the purest products to grey, beige or green for others.

3. TEST TRIALS

3.1. Odour

Bentonite should not have any undesirable odour (e.g. no mould) and should not change the taste of wine.

3.2. pH level

Shake 5 g of bentonite with 100 ml of distilled water for 5 minutes. Allow to stand for 1 hour. Measure the pH level of the supernatant liquid. Natural calcium betonites have a neutral pH level around 6.5 to 8.5. Natural sodium or activated calcium betonites have

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003

a much more alkaline pH level around 8.5 to 10.0.

3.3. Loss during desiccation

The desiccation of 5 g of bentonite at 105°C during 4 hours causes a weight loss of 5% to 15% of the initial weight (often around 10%).

3.4. Preparation of the test trial solution

Weigh p g of bentonite containing 10 g of anhydrous bentonite.

In a 500 ml flask with a large opening which can be hermetically sealed, add 100 ml of tartaric acid solution to 5 g per litre until the solution has a pH level of 3 (R). Sprinkle the bentonite trial sample in the constantly shaken solution (for example using a magnetic stirrer) and a funnel. After this addition, shake vigorously for 5 minutes. Allow to stand for 24 to 48 hours. Decant, centrifuge or filter if necessary to obtain at least 100 ml of clear liquid.

All the following set limits for bentonite are for the weight of dried bentonite.

3.5. Montmorillonite content

Minimum rate:

Manufacturer indicates that the content should not be under 80% by x-ray diffraction analysis.

3.6. Different forms of free silica content

Crystal silica content must be less than 3% (quartz N° CAS 14080-60-7, cristobalite N° CAS 14464-46-1).

Particle holdings under 10 microns must be less than 10%.

Respirable crystal silica content must be under 0.3%.

These standards must be written on the security form supplied by the manufacturer.

3.7. Lead

In the test trial solution (3.4) determine the lead content using the method described in Chapter II.

Lead content must be less than 5 mg/kg.

3.8. Mercury

Determine the mercury content according to the method described in Chapter II with the test trial solution (3.4).

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003

Mercury content should be less than 1 mg/kg.

3.9. Arsenic

Determine the arsenic content of 5 ml of test trial solution (3.4) according to the method in Chapter II.

Soluble arsenic content should be less than 2 mg/kg.

3.10. Iron

Add 12.5 ml of water, 1 ml concentrated hydrochloric acid (R) and 2 ml of potassium thiocyanate at 5% (R) to 5 ml of the test trial solution (3.4). The red coloration should be lighter than what is obtained when using 2.5 ml citric acid at 5% at pH 3 (R), 1 ml concentrated hydrochloric acid (R), 15 ml of iron salt solution (III) at 0.010 g of iron per litre (R) and 2 ml of potassium thiocyanate solution at 5% (R).

Iron content should be less than 600 mg/kg).

Iron can also be determined by atomic absorption spectrometry according to the method in Chapter II.

3.11. Aluminium

On the test trial solution (3.4), find extractable aluminium according to the method described in Chapter II.

Extractable aluminium content should be less than 2.5 g/kg.

3.12. Calcium and magnesium

On the test trial solution (3.4), determine calcium and magnesium using the methods outlined in the Compendium of International Methods of Analysis of Wine and Musts.

Calcium and soluble magnesium combined should be less than 100 meq for 100 g.

3.13. Sodium

On the test trial solution (3.4), determine sodium using the method outlined in the Compendium of International Methods of Analysis of Wine and Musts.

Soluble sodium content should be less than 10 g/kg for natural bentonites and less than or equal to 35 g/kg for activated bentonites.

3.14. Presence of large particles

Put 1 litre of water in a 1.5 litre long stem glass. Slowly add while shaking the liquid, a quantity of bentonite corresponding to 50 g of dried bentonite. Shake vigorously 2 to 3

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003

minutes and allow to stand for 24 hours. Shake 2 to 3 minutes and allow to stand for 2 minutes. Using a siphon, take off 9/10 of the cloudy liquid exceeding 100 ml and leave the deposits at the bottom of the glass. Add 900 ml of water. Shake 1 minute. Allow to stand for 2 minutes and repeat to obtain 5 washings. Remove the deposit and put in a capsule. Dry and weigh. The residue must be less than 8 g for 100 g.

3.15. De-acidification tests trials

Weigh (p) of bentonite containing 0.2 g of dried bentonite. Put this in a 125 ml flask containing 50 ml of citric acid 0.033 M solution (R). Shake vigorously for 5 minutes and allow to stand for 30 minutes. Either filter or centrifuge. Take 10 ml of filtrate and titrate with an acid solution of 0.1 M of sodium hydroxide with a drop of phenolphthalein solution (R), that is n ml the volume poured to obtain a colour change in the indicator:

250 (10 – n) is the number of milliequivalent of acids fixed or neutralised for 100 g of bentonite.

The maximum limit is 2.5 eq/kg.

3.16. Rate of swelling

Swelling indicator: specific test is necessary.

2 g of bentonite is strewn over 100 ml of demineralised water and 100 ml of wine in a graduated test tube cylinder. After 24 hours, weigh the volume of bentonite. This will be expressed in ml/g of dried product.

3.17. Protein adsorption test trial (for bentonite to go through deproteinisation)

3.17.1. Preparation of test trial solution:

Mix 5 g of egg white with a sufficient amount of citric acid solution of 5 g per litre (pH=3) to make 1 litre. Filter. Determine total nitrogen on 100 ml of this solution by using the procedure described in Chapter II. This solution contains approximately 90 mg of total nitrogen for 575 mg of proteins per litre.

3.17.2. For each test trial

Using 100 ml of this solution, mix increasingly larger doses of bentonites prepared in a 5% suspension in order to process doses of 0.1 to 0.8 g/l. Shake vigorously and maintain at 15°C–20 °C for 6 hours. Centrifuge and proceed with determinations of nitrogen or residual proteins.

A de-proteinising bentonite should eliminate at least 50% of the proteins in a

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003

synthetic solution with a 0.4 g/l dose.

3.17.3. Determining the specific adsorption surface

(or the adsorption indicator for methylene blue)

See method described in annex.

The accepted limit should be 300 mg/100g.

4. STORAGE

Bentonites must be stored in a ventilated area in watertight containers away from volatile objects that they could adsorb.

ANNEX

DETERMINATION OF THE SPECIFIC SURFACE OF ADSORPTION OF BENTONITE

1. GENERAL INFORMATION

1.1. Aim of the test trial

This test trial enables to measure the capacity of bentonite to adsorb methylene blue.

Clays, organic matters, and iron hydroxide preferentially adsorb methylene blue. This capacity takes into account the activity on the surface of these elements. We call, “blue value” of bentonites, the quantity expressed in grams of methylene blue adsorbed per 100 g of bentonites.

1.2. Principle of the test trial

Elemental doses of a methylene blue solution are injected successively into an aqueous solution containing the trial sample. The adsorption of blue is checked after each addition by making a spot on a paper filter (spot test, see paragraph 5).

For a simple conformity check, the specified quantity of blue is injected once.

2. EQUIPMENT AND REAGENT

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003

2.1. A 25 ml burette graduated 1/10 ml.

2.2. Paper filter: quantitative and without ashes (< 0.010); weight: 95 g/m2; thickness: 0.20 mm; filtration speed 75; retention: 8 micrometers.

2.3. A glass rod: 300 mm length; 8 mm diameter.

2.4. A magnetic stirrer and magnetic stirring bar.

2.5. Methylene blue of medicinal quality at 10g/l ± 0.1 g/l.

The maximum duration for using the solution is one month. The solution must be stored away from light.

2.6. Demineralised or distilled water.

3. PREPARATION OF TEST TRIAL SAMPLES

Add 10 g of bentonite in 200 ml of distilled water, allow to swell for 2 hours, then homogenise by shaking.

4. CARRYING OUT TEST TRIAL

4.1. Definition of spot test

After each addition of blue (see paragraph 5.2), this test involves taking a drop of suspension that is placed on a paper filter using a glass rod. The spot that is formed is composed of a central deposit of matter, blue in colour surrounded by a humid colourless area.

The drop must be such that the diameter of the deposit is between 8 and 12 mm.

The test is positive if a persistent light blue ring appears around the middle deposit in the humid zone. The test is negative if the ring is colourless.

4.2. Determination

Using a burette, pour 2 ml of blue solution in a container with 200 ml of suspension of bentonite maintained in agitation. After 2 minutes, add 1 ml of blue solution. This addition is followed by the spot test on filter paper.

Allow the asorption of blue to occur which is not instantaneous. Meanwhile tests

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003

should be conducted minute by minute.

If the light blue ring disappears at the fifth spot, proceed with elemental additions of 0.2 ml of blue and then 0.1 ml.

Each addition is followed by tests conducted minute by minute.

Renew these operations until the test remains positive for 5 consecutive minutes: the determination is considered as ended.

That is V ml poured.

5. EXPRESSION OF RESULTS

5.1. Blue value

The blue value expressed in grams of blue for 100 g of bentonite is shown in the following formula:

V x 10

V is the value of blue methylene poured in ml.

5.2. Conformity check compared to a given specification

The specification is expressed in blue value for 100 g of bentonite, or s of this value.

The volume of blue solution to be added in one time to the preparation (3) is:

The spot test is done after eight minutes of shaking. If it is negative, the bentonite complies with the specification.

Certified in conformity Paris, 19th June 2003
The Director General of the OIV
Secretary of the General Assembly
Georges DUTRUC-ROSSET

© OIV 2003