REDOX ASPECTS ON CERTAIN ANTISEPTIC SUBSTANCES OF OENOLOGIC USE

ASPECTE REDOX ASUPRA UNOR ANTISEPTICI DE UZ OENOLOGIC

ZĂNOAGĂ C. V.[1], COTEA V. V.[2], NICULAUA M.[1]

[1]Research Centre for Oenology - Iaşi branch of Romanian Academy[2]

[2]University of Agricultural Sciences and Veterinary Medicine Iaşi, Romania

Abstract. *The rH values modulated by SO_2 substantiates, by the small values, the anti-oxidizing effect at high concentrations, and by the high values, the bacteria-static effect at small concentrations. The potassium metabisulphite modulates only rH values with effects that tempt the bacteriastasis, as well as the potassium sorbate. But, at the contact of substance with the bios, the rH used as a marker shows that SO_2 is highly labil, and the stability grows in the SO_2–potassium metabisulphite–potassium sorbate series, the latter seeming to be the most proper for the long-term preservation of wine qualities, with no subsequent corrections.*

Key words: SO_2, potassium metabisulphite, potassium sorbate, redox potential

Rezumat. *Valorile rH modulate de către SO_2 exercită, prin valorile mici, un efect antioxidant la concentraţii mari, iar prin valorile ridicate, un efect bacteriostatic la concentraţii mici. Metabisulfitul de potasiu modulează numai valori rH cu efecte ce tentează bacteriostazia, ca şi sorbatul de potasiu. Dar, la contactul substanţelor cu viul, valorile rH, utilizate ca marker, arată că SO_2 este foarte labil, iar stabilitatea creşte în ordinea SO_2–metabisulfit de potasiu–sorbat de potasiu, ultimul părând a fi cel mai potrivit pentru conservarea calităţilor vinului, fără corecţii ulterioare.*

Cuvinte cheie: SO_2, metabisulfit de potasiu, sorbat de potasiu, potential redox

INTRODUCTION

Wine making uses a series substances as preservatives – namely bacteriostatic, sometimes bactericide –, in order to ensure on a longer term the qualities of wine, the product of a technology that entwines with art. Such substances are also used, as additives in the ever more industrialized food that we consume more often and in larger quantities than wine. While in wine making, the use of such substances is strictly regulated, even enacted/institutionalized, tradition also braking/slowing their introduction, use, and ultimately, extension, in the food industry, which lacks a tradition taht gave birth for wine making to that international forum namend “Office international de la vigne et du vin” (notice that in its documents the subject is not only the wine but also anything related to it), the use of such substances often escapes control/surveillance.

That’s why we propose/bring in a study, original in terms of procedure, on these substances, in order to find out or at least assume the side effects on the consumer but also, with direct reference to oenology, on becoming of grapes into wine.

MATERIAL AND METHOD

We chose, subjective, of course, three such substances: SO_2 (E 220), its solid (/potential) form of potassium methabisulphite (E 224), that is, two forms of adding the same active substance (SO_2), respectivelly the sorbic acid (as potassium salt – an esential form for wine, as it brings off a unity between it and the added substance, by means of K^+ ion, but also form reasons as pragmatic as possible, related to the superior/better solvability of sorbate) (E 202), a substance that seems to act on a different way, as it does not liberate SO_2, even more, as it is considered absolutely harmless, metabolizing like any other organic acid (though man does not usually consume sorbic acid, which can be found almost exclusively in the fruits of *Sorbus*, a forest shrub). And we chose, as a new way, but also relying on an ever more enriched data base, to treat the subject as being o redox modulated one. The procedure details are presented in (Duca G.et al., 2001; Zănoagă C. V. et al., 2010).

RESULTS AND DISCUSSIONS

The prototype of this substance class, even in historical terms, is SO_2, also a substance naturally known to wine: during fermentation SO_2 appears as a result of sulphates reduction. It is a substance, as simple in structural terms, as it is physiologically complex: it is bacteriostatic – even bactericide –, but also an antioxidant, that is, mandatory, a reducer. But it also is, in its stable form in water, implicitly accesible to vegetal (in grapes), microbial (yeasts, bacteria) cells, H_2SO_3, that is an acid. This fact is also shown in figure 1 which which, compared to the same order data in (Zănoagă C. V. et al., 2010), suggests a unity in acids manifestation: the ambivalence of a reducing behaviour at high concentrations, respectivelly an oxidizing one at low concentrations.

This fact explains both the antioxidant effect as, even from concentration as low as 1/1,000 (fig. 1 – lg C = –3), SO_2 modulates net reducing rH values (approx. 23), and the inhibitive effect, at least for certain forms of microorganisms, such as molds (compare the rH value of about 23, modulated at 1/1,000 concentration, to the optimum value for *Penicillium*, of about 19 (Duca G.et al., 2001). A light sulphitation helps yeasts in their competition with bacteria (be they acetic), which preffer reducing rH-s: a rH of about 25, ensured by the SO_2 concentration of 1/20,000 (lg C = –3.3) inhibits bacteria, but represents the optimum for yeasts.

The “solid” form of SO_2, the potassium methabisulphite, chosen because the grapes, implicitly the wine, is rich in / compatible with this cation, but meant, in contact with wine acidity, to develop the same SO_2, known as an active antimicrobial, is a substance with reducing (redox) effect: in the studied concentrations (Fig. 2: 1/100 (lg C = –2)…1/1,000,000 (lg C = –6)), the substance develops only the lower level of rH = f(C) dependence.

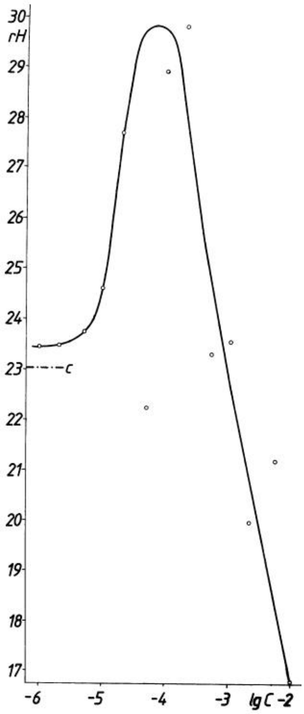

Fig. 1. Dependence rH = f(C) of SO_2

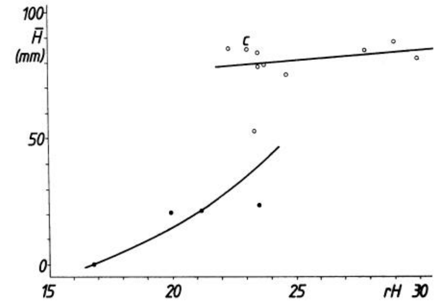

Fig. 4. Dependence of plantlets's average height on rH of SO_2 solutions

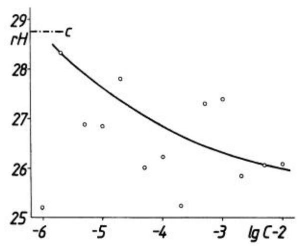

Fig. 2. Dependence rH = f(C) of potassium methabisulphite

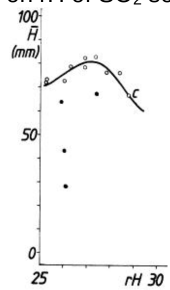

Fig. 5. Dependence of plantlets's average height on rH of potassium methabisulphite solutions

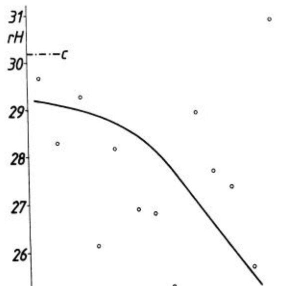

Fig. 3. Dependence rH = f(C) of sorbic acid

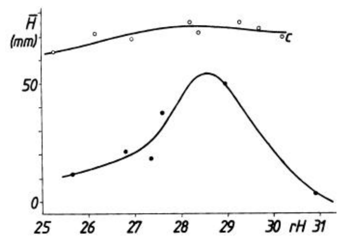

Fig. 6. Dependence of plantlets's average height on rH of sorbic acid solutions

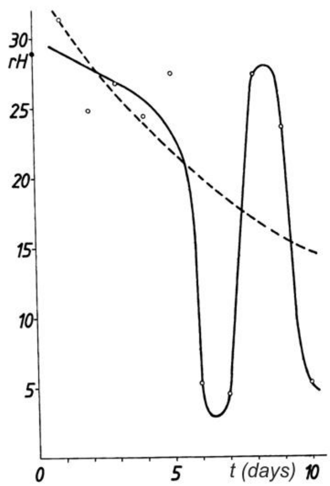

Fig. 7. Dynamics of substrate's rH in SO_2 case

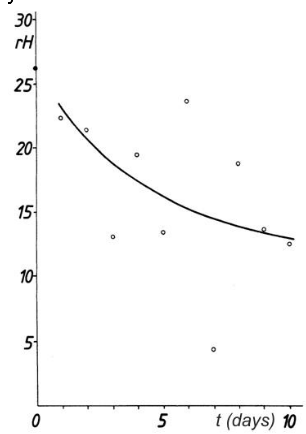

Fig. 8. Dynamics of substrate's rH in potassium methabisulphite case

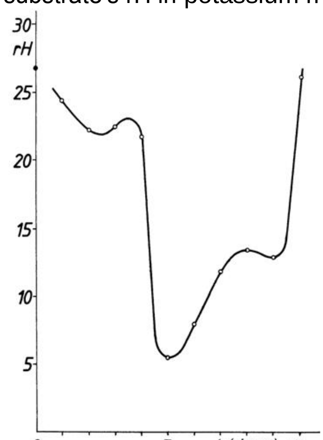

Fig. 9. Dynamics of substrate's rH in sorbic acid case

The effect of this substance is questionable/controversial even if, by means of a chemical becoming,it would develop that SO_2 which could materialize the mechanism described before.

The sorbate (potassium, from the same reasons) (fig. 3) seams to be more "intelligent": at high concentrations (approx. 1/100 – lg C = –2), it modulates optimum for yeasts but absolutely awkward for bacteria rH values, but at lower concentrations induces rH values which are awkward to any heterotroph; so it results an obvious preservative action.

The effect of redox modulation is felt differently at the level of a test plant – wheat – but in conditions that promote heterotrophy. That is, at high concentrations (up to 1/2,000) (fig. 4 – the full dots), SO_2 induces a semi-Gaussian shape/allure of the biological effect (seedlings height, $\overline{H}$), proving the redox modulation. For lower concentrations (the empty dots), no clear dependence is seen, but only a slight tendency of stimulation at oxidizing values of rH (otherwise, a normal behaviour for plants). In other words, at such concentratios, the SO_2 effect is of a different nature than the redox one. This fact can be attributed to the presence of SO_2 in a free form, the H_2SO_3 compound it could form being unstable. As it is more stable, the potassium methabisulphite (fig. 5) shows an obvious redox dependence (a Gaussian shape), from which are excepted only the high concentrations (up to 1/1,000) which can be accused of osmotic or simply toxicological mediated effects. The potassium sorbate proves to be even more redox modulating. Analyzing figure 6 only a disjunction between the high concentrations (up to 1/5,000 – the full dots) and the low ones it can be seen, in both cases being seen tipical, Gaussian, dependencies, a more obvious one at high concentrations and a more discreet one at low concentrations.

As regards the stability of substances depending on the environment (the experimental details are identical with those mentioned in (Zănoagă C. V. et al., 2010), SO_2 proves to be, one more time, the most sensitive, "personality"-lacked, substance, as proven by figure 7: after a period of relative stability, the appear large oscillations of rH (the full line), and only the average (the dashed line) shows a progresive reduction, accordingly to the effect of seedlings living in contact with the SO_2 solution, a sign of losing in time the redox effect specific to the substance.

It is something normal, as long as the more stable form of SO_2, that is the potassium methabisulphite, shows the same becoming of the substance (fig. 8). The most obvious/apparent redox modulator, that is potassium sorbate, also shows the best resistance to the action on test-organism – wheat –, able to counteract the presence of the redox modulating substance redox effect (fig. 9): after a quite long time of rH constancy, that is of "personality", there follows a loss of it in the favour of the contact organism effect, so that at the end of the experiment, when the test-organism becomes allelopathic inhibited, the substance "personality" enforces again, by the means of rH returning to the previous value.

CONCLUSIONS

The potassium sorbate has the most obvious preservative effect on a long term scale, it also being the substance which, through a redox mechanism, controls – no matter the scale of concentration – the becoming of the existing organisms in wine. In other words, the potassium sorbate can be applied/introduced as result of an appropriate study, valid forever, while SO_2 or the potassium methabisulphite needs a continuous watch and corrections in order to maintain the preservative effect.

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