

Study of the Acidification of Sherry Musts With Gypsum and Tartaric Acid

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Must acidification is a necessary operation in hot regions due to the low natural acid content of the grapes grown there. Tartaric acid is what is most usually used for this purpose. Using gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) allows the amount of tartaric acid needed to reach a given pH to be reduced. This paper is a study of the acidification of musts produced in Sherry area (Southern Spain) to a pH of 3.25 with tartaric acid alone and tartaric acid acting together with 2 g/L of gypsum. Using gypsum causes a reduction in must pH of approximately 0.2 units and allows the tartaric acid dosage to be cut down by 1.5 to 2.5 g/L. The concentration of sulfates in the fermented wine lies below 2.5 g/L (the maximum authorized by the European Community), and the calcium concentration is 130 mg/L. Both levels are compatible with a correct winemaking. The acid buffering power of the wine and the alkalinity of the ash are reduced by the use of gypsum, which makes later acidification easier. Other wine component levels are not affected.

KEY WORDS: gypsum, tartaric acid, sherry must, must acidification

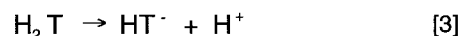
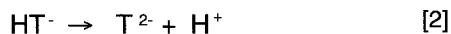
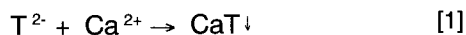
Gypsum treatment is a traditional enological practice consisting in adding gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to the must prior to fermenting, and it is aimed at cutting down the must's pH.

Though references to the use of gypsum in wine-making date back as far back as to the Roman age (11), few in-depth studies have been made of the subject. Fernández de Bobadilla *et al.* (6) have studied the use of gypsum in sherry grapes and musts, produced in Southern Spain, referring to the mechanisms whereby gypsum operates and the effects it produces.

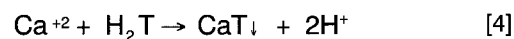
The effect of the CaSO_4 in the must is based on the displacement of the ionic balances produced by the Ca^{+2} ion. This intervenes in the precipitation balances of two salts of limited solubility, namely the CaSO_4 itself ($K_{\text{SP}} = 6.1 \cdot 10^{-5}$) and the calcium tartrate ($\text{Ca}(\text{C}_4\text{H}_4\text{O}_6)$ or CaT) ($K_{\text{SP}} = 7.7 \cdot 10^{-7}$). However, in affecting one of the ionic forms of the tartaric acid, it originates a redistribution of the others, according to the dissociation constants of this acid ($K_1 = 1.04 \cdot 10^{-3}$; $K_2 = 4.55 \cdot 10^{-5}$).

The gypsum dissolves until the CaSO_4 and CaT solubility products are satisfied. Because the latter is much less soluble than the former, CaT precipitation occurs. To replace the T^{2-} eliminated, part of the HT^- is dissociated and this in turn is replaced by another from the dissociation of the H_2T .

The sum of the different ionic reactions considered:



originates the following overall reaction



showing the two H^+ which explains the reduction of pH due to the presence of the gypsum in the must.

The buffering power of the must depends on the concentration of its different tartaric acid fractions according to the following expression:

$$\text{Buffering power} = \frac{d\text{Ac}}{d\text{pH}} = 2.306 \frac{[\text{HA}] [\text{A}^-]}{[\text{HA}] + [\text{A}^-]} \quad [5]$$

where has been assumed, as a simplified treatment, that the tartaric acid is monoprotic.

The buffering power will be affected differently depending on whether acidification is performed using gypsum or tartaric acid. Indeed, the increase caused in the $[\text{HA}]$ fraction by the addition of tartaric acid should affect the numerator more than the denominator in expression [5], causing an increase in the buffering power. Similarly, the decrease in $[\text{A}^-]$ brought about by adding gypsum will cause a decrease in buffering power.

Fernández de Bobadilla *et al.* (6) use a dose of 3 g/L of gypsum and observe a pH drop of 0.2 units, a slight increase in the titration acidity, and a reduction in the alkalinity of the ash and tartrate, malate and citrate anions.

González Gordon (8) fully describes gypsum-treating operation in the Jerez area. Jeffs (9) provides data on the composition of musts and lees from musts treated and not treated with gypsum. Pato (10) submits useful formulas and tables for acidifying with gypsum and tartaric acid (hereinafter referred to as H_2T).

The European Community's generic regulation over wines (3) authorizes only 1.5 g/L H_2T for acidifying musts and 2.5 g/L for acidifying wines.

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The European liqueur wines regulation (4) allows the use of gypsum in full-bodied wines and full-bodied liqueur wines, provided that the residual sulfate content, expressed as K_2SO_4 , is less than 2.5 g/L. These wines may take supplementary acidification with 1.5 g/L of H_2T during winemaking.

Gypsum use is also authorized in the U.S.A. for producing wines aged under a film of flor yeast (1), though there, the residual sulfate content cannot exceed 2 g/L.

Materials and Methods

Description of the winemaking method: The must was obtained in a press house within the production area of the Jerez-Xérèz-Sherry appellation d'origine, Southern Spain, in September 1990. The grape used was Palomino Fino from the zone known as Balbaina¹ (8).

The must was obtained in 8000-L Vaslin platen presses, using the fraction obtained at a pressure of under 1.0 Atm. The must was treated with 100 mg/L of SO_2 and then acidified with gypsum and H_2T (hereinafter referred to as gypsum-treated must) or H_2T alone (hereinafter referred to as tartarized must). It was allowed to settle at room temperature for 12 hours in 30 000-L vertical tanks. Afterwards the solids-free fraction was drawn off to a 20 000-L fermenting tank, and seeded with 3% of pure yeast culture carrying selected *Saccharomyces cerevisiae*, and it was fermented at a controlled temperature of 25°C.

When fermentation ended, the must was kept in the tank until December, when the first drawing off, or deslío², was performed, adding alcohol to make for a alcoholic degree of 15% volume according to traditional usage in fino-type sherry winemaking (2) (8).

Preparation of must samples for analysis: The samples of musts before fermentation were taken in the 30 000-L tanks just one hour after addition of the acidifier. The samples after fermentation were taken in the 20 000-L fermentation tanks.

These samples were centrifuged and degassed with ultrasound to eliminate CO_2 (the fermented samples only). Next they were filtered through an 8- μ m membrane, and the samples that were to be put through HPLC were furthermore filtered through a 0.22 membrane.

Definitions

¹**Balbaina:** Zone in the Jerez area (within the municipality of El Puerto de Santa María) renowned as the producer of the best fino-type wines.

²**Deslío:** Traditional operation in sherry wine wine-making, consisting in separating the fermented must from the lees and adding alcohol up to the alcohol content at which aging will take place.

³**Fino:** Sherry wine matured biologically under a film of yeasts.

Reagents: The gypsum used in testing was of food-industry quality. All reagents were analytic-grade. For HPLC analyzing, HPLC-grade reagents were used.

The water for preparing solutions and controls was bi-distilled and purified by reverse osmosis (Millipore Milli Q Plus™ system).

Analytic methods Alcohol content, pH, titratable acidity, volatile acidity, potassium, calcium, sulfates, ash, and ash alkalinity were analyzed using official E.C. analysis methods (5).

The buffering power was determined by titration up to pH = 4 with 0.1 N NaOH. The results are given in meq/L \times unit pH.

Tartaric acid was determined by HPLC according to (7), with some slight modifications. The chromatographic columns used were four Waters Fast Fruit™ and one IC-PAK™ Ion-exclusion columns connected in series. Detection was performed at 214 nm.

Equipment: Equipment used was as follows:

pH meter: Orion Research Mod. 811.

Atomic absorption spectrophotometer:
Perkin-Elmer Mod. 372.

Liquid chromatograph: Waters, with
990 photodiode-array detector.

Results and Discussion

Analytic characteristics of the musts used:

The figures given in Table 1 are typical of the musts from the Balbaina area, which lies near the sea and produces musts with a low sugar content and light wines suitable for making fino-type³ sherry wines (2) (8).

Table 1. Analytical characteristics of musts.

Samples ^a	Be	pH	Tit. acid (g/L TH_2)	Total SO_2 (mg/L) ²
1 to 7	10.5	3.64	3.52	124
8 and 9	10.4	3.78	3.90	124
10 and 11	10.3	3.78	3.26	124
12 and 13	10.7	3.83	3.60	124

^a Description of Samples:

Samples 1-5: Dosage determination tests.

Samples 6-9: Real testing on acidification with gypsum and tartaric acid.

Samples 10-13: Real testing on acidification with tartaric acid.

Composition of the gypsum used: The standard analysis of the gypsum used in this experiment was as shown in Table 2. This table shows that impurities were no more than 0.75%.

Testing to determine $CaSO_4$ and H_2T dosages: In order to find out what amounts of acidifiers are necessary, a prior experiment was run on 12 L volumes of must from the first test tank. The acidification processes tested, employed 1, 2, and 3 g/L of gypsum along with an H_2T quantity to pH = 3.25. A control-test with only H_2T was also carried to the same final pH level, and

Table 2. Gypsum composition (data given in %).

Free water	0.05
Combined water	19.33
Silica (SiO ₂)	0.16
Ferric oxide (Fe ₂ O ₃)	0.12
Calcium oxide (CaO)	33.94
Magnesium oxide (MgO)	0.47
Sulfur trioxide (SO ₃)	45.18

Table 3. Pinpointing acidifying dosage.

Test no.	SO ₄ Ca g/L ^a	pH ^b	H ₂ T g/L ^c	Ca mg/L	K mg/L	H ₂ T g/L	Buff. ^d power
1	0	3.64	0	140	1913	7.19	33.32
2	1	3.54	2.66	270	1904	9.81	50.12
3	2	3.45	1.93	330	1921	8.73	43.75
4	3	3.38	1.28	425	1930	7.09	38.23
5	0	3.64	3.12	140	1887	10.45	53.83

^aGypsum dose added.

^bpH after gypsum.

^cH₂T dose needed to adjust pH = 3.25.

^dBuffering power (meq/L x unit pH).

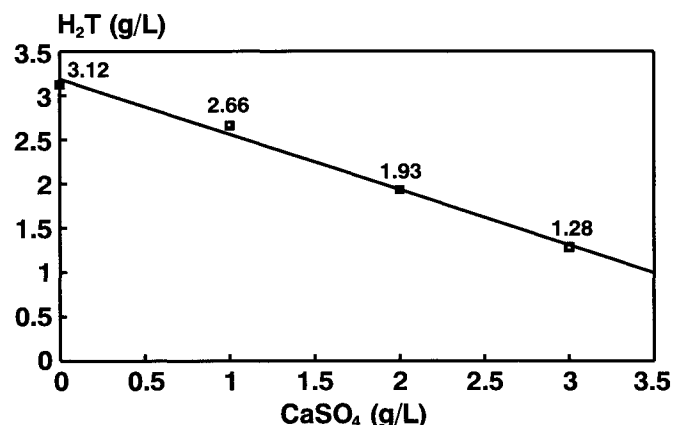
lastly, there was another control-test that was not acidified at all. The results are given in Table 3 and Figures 1 and 2.

The dose of gypsum chosen for testing at the real scale was 2 g/L, adjusting the final pH to a level of 3.25 with H₂T. Thus the drops in pH caused by both acidifiers are approximately 0.2 units.

These tests were fermented, and their study was continued until after racking (Deslío).

Determination of reaction time: A trial was carried out to find the time necessary for the reaction to reach its conclusion. To do this, 2 g/L of gypsum was added to a 30 000-L tank; it was stirred for an hour and the pH analyzed periodically.

The data are set out in Table 4. As it can be seen there, the reaction is completed in less than ten min-

Fig. 1. Sherry must acidification. CaSO₄ and H₂T dosage for pH = 3.25.

utes. The acidification trial samples were taken one hour after addition of the acidifier, including ten minutes stirring.

Acidification tests.

Before fermenting: The data given in Table 5 show that acidification with H₂T alone, may require doses higher than the authorized 3 g/L (Tests n° 11 and 13). The use of gypsum reduces the necessary dose of H₂T to more moderate levels: 1.3 and 1.7 g/L in tests number 7 and 9. This is a very important reduction in the amount of tartaric acid that must be employed.

pH: The final pH of the acidified musts may be seen to deviate slightly from the initially forecast figure of 3.25, due probably to the difficulty of maintaining in suspension an insoluble solid whose natural tendency is to agglomerate, such as gypsum. This entails a loss in the efficiency of the acidifiers used.

Titratable acidity: The titratable acidity of the gypsum-treated musts may be observed to be an average of 1.72 g/L lower than that of the tartarized musts.

Calcium: Part of the gypsum not used in reaction [4] remains in excess, pushing up the calcium levels of the must, as may be observed in Tables 3 and 5. This means an average increase in concentration of 110 mg/L with a dose of 2 g/L of gypsum.

Potassium: The potassium cation goes up slightly in gypsum-treated musts, an average of 35 mg/L, due probably to impurities in the gypsum used in the process. However, in tartarized musts, potassium drops appreciably with the precipitation of potassium bitartrate (hereinafter referred to as KHT). The same occurrence may be observed in the data from Table 3.

Buffering power: In tartarized musts, the buffer-

Table 4. pH Variation over time.

pH	Time (min)
3.71	0
3.61	1
3.59	2
3.57	3
3.56	4
3.55	5
3.54	6
3.54	7
3.53	8
3.52	9
3.52	10
3.51	15
3.52	30
3.53	45
3.52	60

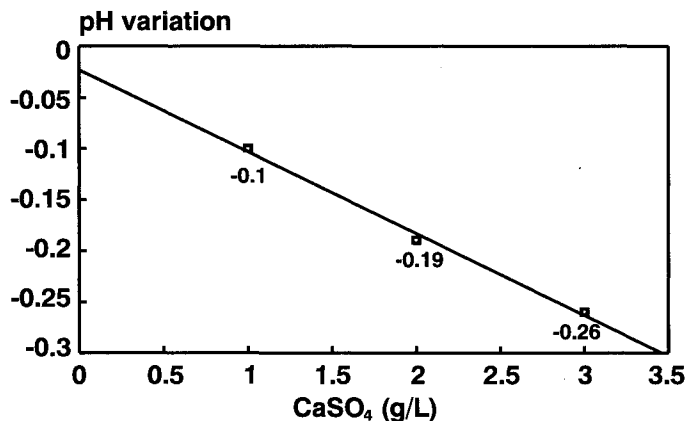
Fig. 2. Sherry must acidification. pH variation with CaSO₄.

Table 5. Analytical characteristic of acidified musts before fermentation.

Test no. ^a	CaSO ₄ g/L ^b	H ₂ T g/L ^c	pH ^d	TA g/L TH ₂	Ca mg/L	K mg/L	H ₂ T g/L	Buff. ^e
6	0	0	3.64	3.52	140	1913	7.19	33.32
7	2	1.30	3.29	4.35	255	1955	7.90	37.50
8	0	0	3.78	3.90	150	2009	7.68	34.44
9	2	1.70	3.26	5.25	255	2037	8.55	39.80
10	0	0	3.78	3.26	140	1955	7.05	37.20
11	0	3.83	3.34	5.62	140	1904	9.49	50.00
12	0	0	3.83	3.60	170	2294	11.10	40.00
13	0	4.25	3.30	7.42	170	1991	12.45	54.81

^aTests 6, 8, 10 and 12 were run on the musts before they were acidified. Tests 7, 9, 11 and 13 were run on the musts after they were acidified.

^bCaSO₄ dose.

^cH₂T dose needed to adjust the pH to 3.25 after the addition of gypsum.

^dFinal real pH obtained.

^eBuffering power (meq/L x unit pH).

Table 6. Analytical characteristics of acidified musts after fermentation.

Test no.	CaSO ₄ + H ₂ T ^a	H ₂ T ^b
	14	15
Alcohol (% vol)	10.2	10.3
pH	3.19	3.23
TA (g/L H ₂ T)	5.50	5.94
VA (g/L acetic acid)	0.20	0.1
SO ₄ ⁻ (g/L K ₂ SO ₄)	2.20	0.58
Ca (mg/L)	130	85
K (mg/L)	1427	1162
H ₂ T (g/L)	3.44	3.88
Buffering power ^c	36.08	40.3
Ash (g/L)	3.52	2.63
Ash elk (meq/L)	19.65	25.08
Dry extract (g/L)	22.3	22.5

^aGypsum-treated must.

^bTartarized must.

^cBuffering power: expressed as meq/L unit pH.

Table 7. Calcium content variation during winemaking (mg/L).

Time (months)	Sample number				
	1	2	3	4	5
1	55	120	140	165	110
4	50	90	120	157	67
8	50	85	115	150	62

Description of samples:

Sample 1: Dosage determination test. Control-test not acidified. After fermenting.

Sample 2: Dosage determination test. Acidified with 1 g/L of gypsum + tartaric acid to pH = 3.25.

Sample 3: Dosage determination test. Acidified with 2 g/L of gypsum + tartaric acid to pH = 3.25.

Sample 4: Dosage determination test. Acidified with 3 g/L of gypsum + tartaric acid to pH = 3.25.

Sample 5: Dosage determination test. Acidified with tartaric acid to pH = 3.25.

Table 8. Potassium content variation during winemaking (mg/L).

Time (months)	Sample number				
	1	2	3	4	5
1	1353	1279	1573	1934	1200
4	1100	750	983	1150	617
8	1000	700	900	1050	600

Description of Samples:

Sample 1: Dosage determination test. Control-test not acidified. After fermenting.

Sample 2: Dosage determination test. Acidified with 1 g/L of gypsum + tartaric acid to pH = 3.25.

Sample 3: Dosage determination test. Acidified with 2 g/L of gypsum + tartaric acid to pH = 3.25.

Sample 4: Dosage determination test. Acidified with 3 g/L of gypsum + tartaric acid to pH = 3.25.

Sample 5: Dosage determination test. Acidified with tartaric acid to pH = 3.25.

ing power increases an average of 13.8 units, while in gypsum-treated musts it increases only 4.8 units. This implies that treating with gypsum decreases must buffering power, as has already been shown.

Acidification tests. After fermenting: The appearance of alcohol in the medium during fermentation decreases the solubility of KHT and prompts heavy precipitation of this salt. The magnitude of KHT precipitation is greater in tartarized musts due to the greater surplus of HT⁻ ions present in the medium. This phenomenon conditions the evolution of most significant tested components of the wine shown in Table 6.

pH and titratable acidity: A considerable reduction in both may be observed, due to the precipitation of KHT. The titratable acidity figures for wines made from musts acidified in both fashions end up being nearly equal after fermentation.

Sulfates and calcium: As was to be expected, both sulfates and calcium are greater in the wine made from gypsum-treated musts. Sulfates do not exceed the legal limit of 2.5 g/L.

Potassium and tartaric acid: The greater amount of KHT precipitation in tartarized musts causes an important reduction in these two items in those wines. The potassium concentrations of tartarized wines are much lower than those of gypsum-treated wines. The H₂T concentrations end up nearly equal, while before fermentation they were much higher in tartarized musts.

Buffering power: The figures for this item are lower than the pre-fermentation levels, also due to the precipitation of KHT, as commented above. The descent is greater in tartarized musts.

Ash and ash alkalinity: The higher ash content of wines made with gypsum-treated musts is due to the fact that here two moles of KHT originate one mole of K₂SO₄. The former, as ash, forms K₂CO₃ (138.2 g/mol), and the latter (174.2 g/mol) is not modified when ash forms.

Alkalinity goes down in gypsum-treated musts, since the K₂SO₄ formed does not cause alkalinity.

Dry extract: The addition of H₂T is compensated by a greater precipitation of KHT in tartarized musts, so the figures for this item are similar in both wines.

Calcium evolution: The calcium content goes down during the first few months after fermenting, as seen in Table 7. In test number 3 (treated with 2 g/L of gypsum), the reduction was 25 mg/L by the end of 8 months, reaching a final concentration of 115 mg/L, which cannot be considered excessive.

Potassium evolution: The content of this cation decreases appreciably after fermenting, as seen in Table 8. In gypsum-treated musts, potassium content remains steadily higher than in tartarized musts, and may be 50% greater by the end of eight months. This effect is due to the greater extension of KHT precipitation in tartarized musts.

An excessive reduction of the potassium content may result in unbalanced wines and an excessively low cationic content after a long period of aging.

Cost of acidification: The price of the gypsum used herein was 0.23 dollars/kg, while the tartaric acid cost 6.08 dollars/kg. With the dosages of gypsum and tartaric acid displayed in Table 4, the cost of the acidification operation in each case was then:

Tartarized:

$$4.04 \text{ kg}/1000 \text{ L} \times 6.09 \text{ \$/kg} = 24.59 \text{ \$/1000 L}$$

Gypsum-treated:

$$1.5 \text{ kg}/1000 \text{ L} \times 6.09 \text{ \$/kg} + 2 \text{ kg}/1000 \text{ L} \times 0.23 \text{ \$/kg} = 9.59 \text{ \$/1000 L}$$

With the official price of fermented musts at 622,61 dollars/1000 L the cost of tartarizing is 3.95% of the must price, while gypsum treating is only 1.54%, which means a considerable saving.

Conclusions

The acidification of sherry musts with 2 g/L of gypsum to complement acidification with tartaric acid produces a decrease of 0.2 units in pH and a reduction of 1.5 to 2.5 g/L in the dose of complementary tartaric acid. This allows the wine to reach logical pH levels without requiring excessively heavy doses of tartaric acid, which in some cases would overstep the maximum authorized dosage. Musts acidified with gypsum and tartaric acid produce balanced wines with moderate acid and cationic contents.

Sulfate concentrations in wines made from gypsum-treated musts do not exceed 2.5 g/L. The calcium content, somewhat high at first, drops considerably after fermentation.

Thus, acidification of musts with gypsum and tartaric acid is a recommendable practice for wines having a low natural acidity, such as sherries.

It would be advisable to complement this paper with a study of the subsequent evolution of calcium and sulfate ions during the lengthy sherry wine aging process.

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