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Objective measurement of

As soon as vintage or must are traded, the problem of objective pricing becomes an issue. The same applies in setting fair but incentive payments between growers and cooperatives. Fourier Transform Mid-Near-Infra-Red (FT-MIR) and the FOSS GrapeScan can help to find a solution.

Whilst the quality of finished wines can already be comprehensively assessed by sensory evaluation, up until now degrees Brix has been the only parameter for assessing the quality of grapes and must. However, degree of Brix on its own is no longer sufficient to describe actual quality potential. The Department of Viticulture & Oenology at the DLR-Rheinpfalz has therefore lent its support to a Ph D study that evaluates the further development of FT-MIR analysis in determining grape soundness. As soon as vintage or must are traded between grower and winery, the problem of objective pricing becomes an issue. The same applies in setting fair but incentive payments between growers and cooperatives. This is where FT-MIR and the FOSS GrapeScan can help to find a solution.

How sound are the grapes?

A special challenge is presented by determination of just how sound grapes actually are. This is already scarcely implemented by subjective visual inspection of the hand picked grapes. And, in any event, visual inspection and assessment of soundness of the grapes delivered has the disadvantage that fungal infestation can only be identified when infructescence are already formed, whereas its negative impact on grape quality may occur already at a much earlier stage than this. Depending on autumn temperatures, humidity and rainfall, substantial development of wild yeasts, acetic and lactic acid bacteria occurs in rotten grapes, and this can greatly reduce the quality of the fruit regardless of the results of visual inspection. However, FT-MIR analysis, as featured in the FOSS GrapeScan and already in use at many cooperatives, provides a fast and simple means of examining must. Our study investigated the possibilities of this technology in testing grape soundness.

The first stage involved generation of over 1 500 must samples, with exactly defined degrees of rottenness of between 0 and 100 per cent, from healthy and rotten grapes. Unfortunately, neither the soundness index based on Southern French and Spanish grapes, supplied by FOSS, nor the soundness index we ourselves developed, could deliver values that satisfactorily agreed with the degree of infestation determined by visual inspection. In order to resolve why the results of analysis and visual appraisal did not match, we examined the content of 100 per cent rotten grapes shortly after Botrytis infection and again some two to three weeks later. We found that, although the grapes examined had been visually appraised as having an identical 100 per cent degree of rottenness, the glycerol and gluconic acid parameters used in determining rottenness by chemical means varied by up to 400 per cent depending on length of Botrytis infection (see Figs 1 and 2). Whilst a grape with a 10 per cent degree of rottenness and only a short period of infection contained 0.4 g/l glycerol, another grape, also with a 10 per cent degree of rottenness but with a longer period of infection, contained 2.5 g/l glycerol. The decisive factor for the quality of a wine is not the external appearance of the grapes but the effect of rottenness on their composition, and therefore on the wine itself. Thus rotten grapes at a temperature of 25°C at the end of September may contain as much as 1 g/l volatile acidity, while rotten grapes at a temperature of 8°C at the end of October will not show any elevated volatile acid content at all.

grape soundness

Professor Ulrich Fischer

As visual appraisal of grapes is not analytically traceable and therefore cannot monitor actual changes in grape or must composition, grape soundness has been defined analytically since Autumn 2003 by reference to the chemical parameters gluconic acid, glycerol, ethanol, volatile acidity and glucose:fructose ratio. As with wine yeasts, most micro-organisms degrade preferentially glucose. The glucose fructose ratio therefore changes with the degree and period of Botrytis infection. Neither growers nor most wineries are familiar with the interpretation of analytical results other than those for volatile acids. We have therefore defined ranges for each of the parameters to enable classification of grapes according to their soundness. These ranges permit classification according to the classes 'sound', 'slightly noticeable', 'noticeable', 'very noticeable' and 'extremely noticeable'.

It is important to take the overall analysis into consideration. If only its glycerol content is high, this will not reduce the quality of a sample provided that the results for the other parameters are satisfactory low. The practical implementation of analysis results is exemplified by the characterization of a Riesling, Pinot Noir and Pinot Blanc in Table 1.

Here the results for both the Riesling and the Pinot Noir show that they are of significantly lower quality. In addition, the lower tartaric:malic acid ratio for the Pinot Noir also indicates a certain lack of ripeness. In spite of its very high degree of ripeness, the Pinot Blanc is of excellent quality and the soundness parameters are

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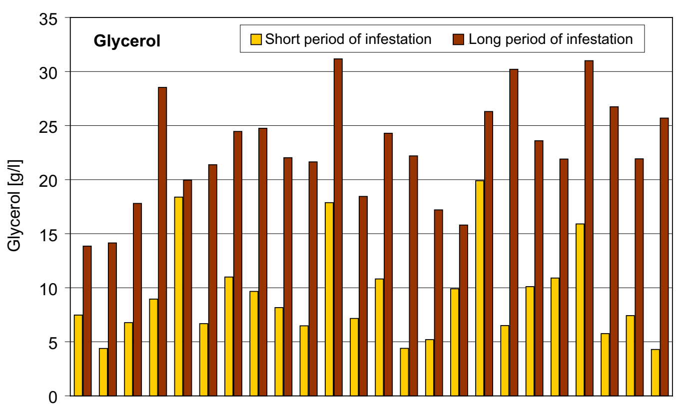

Fig 1: Enzymatically determined levels of glycerol after short (yellow) and long (brown) periods of Botrytis infestation (N=22, vintage 2004)

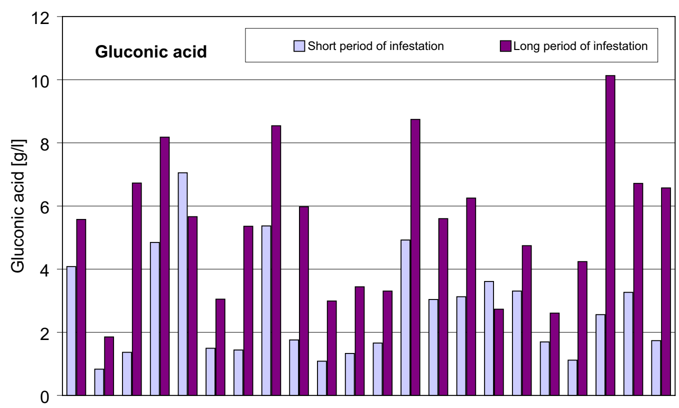

Fig 2: Enzymatically determined levels of gluconic acid after short (blue) and long (purple) periods of Botrytis infestation (N=22, vintage 2004)

FOSS WineScan™ solutions include: WineScan™ Grape for dedicated analysis of grape must

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not particularly high. If we were to use a 'traffic light' system to accentuate critical values, it would be easy to decide whether levels in the wine investigated were noticeable. These musts were separately fermented and there are clear quality defects, in the form of fungal and mouldy taste and lack of fruit distinction, in the Riesling and Pinot Noir, while the Pinot Blanc were of excellent quality.

If grape soundness is to be assessed analytically and the results of that analysis are to affect prices, analysis needs to be precise and reliable. This is much more difficult to achieve in the case of volatile acidity, for example, which occur in only small quantities, than it is in the case of degree Brix and total acid values. Any reliable statement about the quality of a measurement must rely on validation, i.e. an independent verification of the calibration of the analytical instrument using unknown samples that were not employed in its calibration.

The maximum deviation revealed in Table 2 indicates, with a 95 per cent confidence level, the maximum error that can be expected between predicted values and reference values. R^2 describes the correlation between reference values and GrapeScan values. Ideally, where the two values are identical, R^2=1.0. To take maximum deviation into account, threshold values have been assigned to each parameter. In the case of gluconic acid, glycerol and ethanol, a value will only be taken into account if it lies above a threshold of 1 g/l; for volatile acids the threshold is 0.2 g/l.

Nitrogen content and yeast

Nitrogen content is a decisive parameter for completion of the fermentation process and the avoidance of the hydrogen sulphide that is formed when yeasts are not supplied with a sufficient amount of nitrogen compounds and hence will spoil the wine. Its availability is a matter of survival for several generations of yeast, the amount of utilizable nitrogen being in direct correlation to the biomass of the yeast cells. In particular, yeast cells need nitrogen for the configuration of the different enzymes and transporters that keep a neutral pH value within the cell and form active sugar transporters The main sources for nitrogen are ammonium and amino-acids. The latter is also of importance for the formation of the higher alcohols and esters that affect the sensory quality of wines, especially fresh white wines.

Nitrogen content during ripening

Table 3 shows values based on validation of a calibration made in recent years using unknown samples. The parameters measured are those for fermentable amino nitrogen (FAN) derived from amino-acids, nitrogen derived from ammonium and easily assimilated by yeasts and, as the sum of both, total nitrogen. Confidence level is again 95 per cent.

Constraining the examination to ripe grapes, harvested later than 20 September, the standard deviation is reduced considerably (see Table 4). In absolute terms, the concentration of measured nitrogen compound are at the limits of the GrapeScan's analysis capabilities, but their precision is fully sufficient to meet the requirements of wineries.

From Fig 3 it can be seen that ammonium declines as the grapes ripen, while levels for amino-acids increases. The ratio of amino-acids:ammonium is increasing as the grapes ripen (R^2=0,94) and develops parallel to the increasing Brix values (R^2=0,94).

Fig 3 also shows that riper grapes do not necessarily have more utilizable total nitrogen accessible to yeasts, but that there is a clear trend throughout ripening towards more utilizable nitrogen from amino-acids. This may be an indication that the appearance of off-flavour "untypical ageing aroma" (UTA) encountered with unripe vintage is partly the result of a deficiency of utilizable nitrogen from amino-acids. At the same time, the ratio amino-acids to ammonium may be used as a ripeness parameter in the future.

Nitrogen content during fermentation

Nitrogen content in grapes is of primary

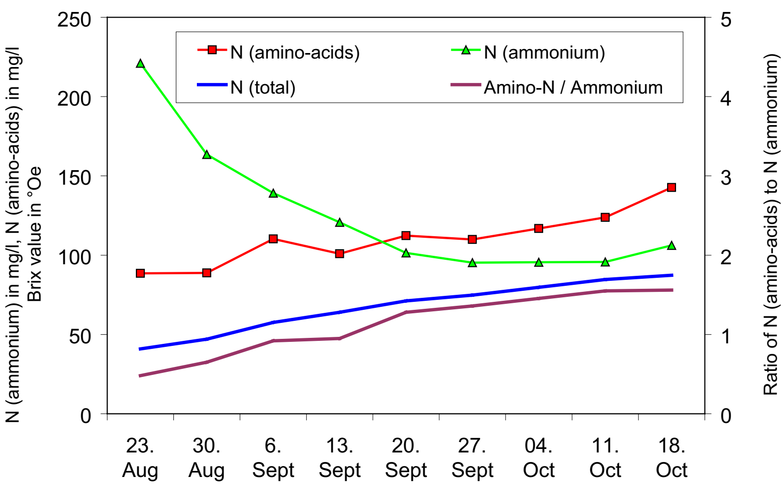

Fig 3: Nitrogen content of grapes during ripening

importance for yeast nutrition. Thanks to the FOSS WineScan it's now possible to check fermentation in each barrel on a daily basis with the help of analysis that's rapid and uncomplicated, allowing winemakers not only to follow the fermentation process exactly in terms of residual sugars, volatile acids, malic and tartaric acid but also to obtain crucial information about the supply of nitrogen to the yeast. This permits early detection of deficiencies and their remedy by addition of ammonium salts, thus avoiding formation of hydrogen sulphide and dealing with stuck fermentations.

Summary

FT-MIR technology now makes possible not only rapid determination of grape composition but also of the metabolic compounds of Botrytis and other moulds, as well as wild yeasts and bacteria in rotten grapes. Simultaneous monitoring of a number of parameters (glycerol, gluconic acid, ethanol and volatile acids) detrimental to later wine quality makes it possible to reach an objective assessment of actual grape quality. The overstepping of ascertained thresholds for those parameters provides effective evidence of loss of quality due to rot.

Visual inspection of grapes for their soundness cannot make any assertions as to those changes in their composition that are decisive for the quality of the wine to be made from them. Now, thanks to FT-MIR, cooperatives and wineries have available to them the instrumentation needed for fast and comprehensive assessment of grape quality at reception. With the help of this technology, an objective pricing basis can be further developed so that operations from vineyard to harvest can be fairly rewarded.

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Table 1: Grape soundness, 2004 harvest

Parameter	Riesling	Pinot Noir	Pinot Blanc
Brix [°Oe]	87	86	111
Ratio tartaric:malic acid	0,7	0,55	0,75
Ratio glucose:fructose	0,95	0,95	0,95
Glycerol [g/l]	3,0	2,1	0,0
Ethanol [g/l]	3,0	2,8	0,5
Gluconic acid [g/l]	3,6	0,1	0,0
Volatile acids [g/l]	0,5	0,2	0,0
Interpretation	**Extremely noticeable**	**Noticeable**	**Sound**

Table 1

Table 2: Agreement between GrapeScan™ and reference methods, analytical parameters for grape soundness

Parameter	Unit	No of samples	Range	R^2	Max deviation[1]
Gluconic acid	g/l	240	0 – 7,0 g/L	0,768	± 1,2 g/l
Glycerol	g/l	255	0 – 7,0 g/L	0,933	± 0,9 g/l
Volatile acids	g/l	58	0 – 1,6 g/L	0,926	± 0,13 g/l
Ethanol	g/l	174	0 – 4,0 g/L	0,849	± 0,8 g/l

[1]expressed as twice root mean square error of prediction (RMSEP x 2)

Table 2

Table 3: Agreement between GrapeScan™ and reference methods, nitrogen parameters, 2004 Harvest

Parameter	Unit	No of samples	Range	R^2	Max deviation[1]
Amino-nitrogen (N-OPA)	mg/l	673	34 – 282	0,889	29 mg/l
Amino-nitrogen (after 20 Sept 04)	mg/l	301	34 – 277	0,956	19 mg/l
Ammonium	mg/l	669	18 – 425	0,974	22 mg/l
Ammonium (after 20 Sept 04)	mg/l	296	18 – 194	0,963	15 mg/l
Total nitrogen	mg/l	669	64 – 515	0,909	48 mg/l
Total nitrogen (after 20 Sept 04)	mg/l	297	64 – 430	0,960	28 mg/l

[1]expressed as twice root mean square error of prediction (RMSEP x 2)

Table 3

Table 4: Agreement between GrapeScan™ and reference methods, fermentation parameters, 2004 Harvest

Parameter	Unit	No of samples	Range	R^2	Max deviation[1]
Amino-nitrogen	mg/l	34	14 – 160	0,820	33 mg/l
Ammonium	mg/l	34	0 – 197	0,959	15 mg/l
Total nitrogen	mg/l	34	15 – 341	0,922	36 mg/l

[1]expressed as twice root mean square error of prediction (RMSEP x 2)

Table 4