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Determination of the titratable acidity and the pH of wine based on potentiometric flow injection analysis

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ABSTRACT

A FIA system using a pH-sensitive detector based on a graphite/quinhydrone/silicone composite electrode was applied to determine sequentially the titratable acidity and the pH of wine, as well as the sum of calcium and magnesium ions. For all measurements the same FIA configuration was used employing different carrier solutions. The results for the determination of acidity and pH are in good agreement with those obtained by classical potentiometric titrations and by pH measurements using a conventional glass electrode. The standard deviation was less than 1.5% for both kinds of measurements and the sample volume was 150 μL. The method allows about 40 determinations of titratable acidity per hour and 30 pH measurements per hour. The titration method can be adjusted to the legal requirements in USA and Europe.

1. Introduction

The determination of pH and titratable acidity of wine plays an important role in the area of oenology, because both parameters affect the properties and quality of wine, esp. the colour and the flavour. Further, the microbiological stability of wine also depends on its acid content. The main acids in wine are tartaric acid and malic acid, and minor constituents are various volatile and non-volatile acids [1].

For the determination of the titratable acidity of wine different procedures are applied. The European standard method is based on the potentiometric titration with a solution of 0.1 M sodium hydroxide to an end point of pH 7. Alternatively, the acidity is determined by titration with bromothymol blue as indicator, especially in case of white wine [2]. In the USA, pH 8.2 is used as end point or phenolphthalein is applied as indicator [3,4]. However, with these methods the true value of the titratable acidity of wine is not measured, because the end point of the acid–base titration is different for each wine. The true end point depends on the composition and concentration of the acids present in the wine sample. Because the acids existing in wine are relatively weak, the real end point will be more alkaline than pH 7.0. Usually the end point varies between pH 7.8 to pH 8.3 [4]. Furthermore, classical acid–base titrations of wine samples are time-consuming and require quite a large sample and titrant volume.

To overcome the drawbacks of the conventional titrations, alternative methods have been described. Berezin et al. gave a review of different methods for the determination of the titratable acidity in various products [5]. For the determination of the titratable acidity in wine some electrochemical methods have been described. Potentiometric measurements with a copper electrode (for the determination of the citric acid content) as well as voltammetric measurements with microelectrodes were suggested [6,7]. Ohtsuki et al. proposed a method based on the voltammetric reduction of quinone [8]. Recently Tôrres et al. suggested a digital image-based method using acid–base titrations without any indicator. Here the pH dependence of the colour change of the anthocyanines present in the wine is exploited for the determination of the titratable acidity. [9] Similar to the classical titrations, there are a few drawbacks of these alternative methods, like large sample and titrant volume, rather long analysis time or the requirement to add supplementary reagents.

To automate the determination of the titratable acidity of wine a number of different flow systems have been suggested [10–17]. These methods are less laborious; however, all of them use photometric detection systems, which cause several problems especially in case of coloured samples like red wine.

Recently, we have introduced a potentiometric detector for FIA titrations based on a graphite/quinhydrone composite electrode [18–21]. These pH-sensitive detectors were characterised by

Abbreviation: EP, equivalence point

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small time constants, sufficient long term stability, a dynamic working range of about 4 orders of magnitude and a detection limit that is almost ten times lower than that of titrations using colour indicators and spectrophotometric detection [22].

In the present study a FIA system using the potentiometric detector was applied to the sequential determination of the titratable acidity and the pH of wine.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. DL-malic acid, potassium chloride, boric acid, phosphoric acid, sodium perchlorate, glacial acetic acid, sodium hydroxide solution (ampules for 1000 mL, $c(NaOH)=0.1$ mol L^{-1} Titrisol®), hydrochloric acid (ampules for 1000 mL, $c(HCl)=0.1$ mol L^{-1} Titrisol®), calcium standard solution ($c=1000$ mg L^{-1}, Certipur®), magnesium standard solution ($c=1000$ mg L^{-1}, Certipur®), Triplex III (ampules for 1000 mL, $c(Na_2\text{-EDTA}\cdot 2H_2O)=0.1$ mol L^{-1} Titrisol®), nitric acid (65%) and hydrogen peroxide (30%) were purchased from Merck, Germany. Sodium hydroxide pellets were from Sigma Aldrich, Germany. Wine samples were purchased from local supermarkets. For all solutions ultrapure water was used (arium 611 UV, Sartorius, Germany).

2.2. Batch measurements

Conventional pH measurements and potentiometric titrations were performed using a pH meter set Qph 70 (VWR international GmbH, Germany) including a glass electrode in conjunction with a pH meter. All batch titrations were performed as follows: at first the wine sample was purged with nitrogen for 10 min to eliminate carbon dioxide. After the purging, an aliquot of 10 mL wine was titrated using a solution of 0.1 mol L^{-1} NaOH as reagent, and the pH was measured after each addition of NaOH to the wine sample.

For redox potential measurements a platinum electrode (Meinsberger Forschungsinstitut, Germany) was used as working electrode and a Ag/AgCl electrode in 3 mol L^{-1} KCl (Metrohm, Switzerland) with an electrode potential of $E=207.0$ mV at 25 °C served as reference electrode. Before redox potential measurements, 40 mL of the sample solution were purged with nitrogen for 30 min. Then, a solution of 0.5 M NaOH was added to the sample solution successively and the redox potential was measured after each addition, respectively. During the whole procedure the sample solution and also the 0.5 mol L^{-1} NaOH solution were purged with nitrogen to exclude the influence of oxygen on the redox potential.

2.3. FIA measurements

2.3.1. FIA configuration

A single line FIA configuration was used. The carrier stream was propelled with a peristaltic pump (ISMATECH, Switzerland) with a flow rate of 1.75 mL min^{-1}. A 6-port-valve (Rheodyne, USA) was used to inject the sample volume of 150 μL into the carrier stream. The construction of the indicator electrode including the preparation of the pH sensitive layer was described earlier [21]. To obtain a flow-through channel with a diameter of 0.5 mm, a hole was punctured through the pH-sensitive layer using a cannula (outer diameter: 0.5 mm). The pH-sensitive detector was connected with the 6-port-valve via a 10 cm long tube (inner diameter 0.5 mm). As reference electrode a saturated Ag/AgCl electrode (DPST Behnert GmbH, Germany) with an electrode potential of $E=197$ mV at 25 °C was used. The Ag/AgCl electrode was connected with the system via a salt bridge as described in [21]. Chronopotentiometric measurements were performed using an AUTOLAB with a PSTAT10 (Ecochemie, The Netherlands) in conjunction with a personal computer. Data acquisition rate was chosen as 5 points per second.

2.3.2. FIA titrations

A solution of 5×10^{-3} mol L^{-1} sodium hydroxide and 1×10^{-2} mol L^{-1} potassium chloride was used as carrier solution for the determination of titratable acidity. The sodium hydroxide concentration was chosen to obtain a convenient dynamic working range. Potassium chloride was added to achieve a sufficiently high conductivity which provides a smooth baseline and thus a good signal-to-noise ratio [23]. Solutions of DL-malic acid in a concentration range from 5×10^{-4} to 1.25×10^{-2} mol L^{-1} were used to calibrate the FIA system. Malic acid was used as it is one of the main acids in wine [1]. 1×10^{-2} mol L^{-1} potassium chloride was added to all calibration solutions to ensure a satisfactory conductivity. The wine samples were purged with nitrogen for approximately 10 min in order to eliminate carbon dioxide before they were diluted and injected into the FIA system.

In case of the determination of the calcium and magnesium content, a solution of 0.02 mol L^{-1} EDTA and 1×10^{-2} mol L^{-1} potassium chloride was used as carrier solution and calibration solutions containing calcium and magnesium ions of 5–30 mg L^{-1} for each ion were used.

2.3.3. FIA pH measurements

As carrier a solution of 1×10^{-2} mol L^{-1} hydrochloric acid and 1×10^{-2} mol L^{-1} potassium chloride was used. The FIA system was calibrated using Britton–Robinson buffer solutions in a pH range from 2 to 8. The Britton–Robinson buffer solutions were prepared as described in [24]. Because of the high ionic strength, i.e., conductivity, of the buffer solutions there was no need to add KCl.

3. Results

3.1. Acid–base titrations

3.1.1. Batch titrations

Conventional potentiometric batch titrations of different wine samples were performed for the sake of comparison. Typical titration curves were obtained. The equivalence point was determined from the root of the second derivative plot of the titration curve, and from the consumption of sodium hydroxide the titratable hydronium ion concentration $c(H_3O^+)$ in the wine sample was evaluated. To calculate the titratable acidity expressed as g L^{-1} tartaric acid the following formula was applied (150.09 g mol^{-1} is the molar mass of tartaric acid) [2]:

$$\text{titratable acidity}\left[g\ L^{-1}\text{tartari acid}\right]=c(H_3O^+)\times\frac{150.09\ g\ mol^{-1}}{2} \quad (1)$$

For each sample three batch titrations were executed. The results are shown in Table 1. The table shows the results of batch titrations (i) for titration until the real equivalence point, (ii) for the titration up to pH 7.0, (iii) for the titration up to pH 8.2.

Neither by titration to an end point of pH 7 nor by titration to pH 8.2 the true value of titratable acidity is determined; in fact the pH of the true end point is different for each wine and lies between pH 7 and pH 8.3 [4]. By analysing the root of the second derivative plot of the titration curve to determine the end point, a good approximation of the true end point is given.

Table 1
Comparison of the results of batch titrations obtained for titration until the real equivalence point (EP), for the titration up to pH 7.0 and for the titration up to pH 8.2.

	Titratable acidity in mmol L^{-1} H_3O^+ (and in brackets in g L^{-1} tartaric acid)		
	EP	**pH 7**	**pH 8.2**
Red wine 1	68.0 (5.10)	66.2 (4.97)	72.0 (5.40)
Red wine 2	63.3 (4.75)	62.6 (4.70)	67.4 (5.06)
Red wine 3	73.8 (5.54)	69.7 (5.23)	75.9 (5.70)
Red wine 4	74.2 (5.57)	71.9 (5.40)	75.8 (5.69)
White wine 1	65.7 (4.93)	63.9 (4.80)	67.6 (5.07)
White wine 2	67.8 (5.09)	65.1 (4.89)	69.1 (5.19)
White wine 3	82.8 (6.21)	78.5 (5.89)	83.2 (6.24)
White wine 4	81.5 (6.12)	78.9 (5.92)	82.6 (6.20)
Rosé wine	63.1 (4.74)	59.6 (4.47)	63.9 (4.80)

3.2. FIA titrations

3.2.1. Matrix simulation of wine

In preliminary experiments with water as solvent, very well reproducible peaks were obtained, but systematic and highly reproducible deviations between the FIA and batch titrations were observed. The main reason for that lies in the fact that wine is a very complex matrix containing constituents which obviously interfere in the sensor response.

To confirm this assumption a white wine sample, an aqueous solution of DL-malic acid and a solution of DL-malic acid dissolved in a white wine titrated to the equivalence point (EP) were titrated with 0.5 mol L^{-1} NaOH and the redox potential was measured after each NaOH addition using a platinum electrode in conjunction with a common reference electrode. The hydronium ion concentration of the DL-malic acid solutions was similar to the hydronium ion concentration in the wine. The redox potential in such a solution must change while malate/oxaloacetate is a redoxsystem the potential of which is dependent on the pH of the solution (hydronium ions are involved in the electrochemical equilibrium).

Fig. 1 shows that the curves of the aqueous solution of DL-malic acid and wine show a similar shape, but the redox potential in dependence of the added NaOH volume is shifted. In case of the wine sample the potential jump at the equivalence point is larger than in case of the aqueous DL-malic acid solution. The differences of the redox potential indicate that additional pH dependent redox systems are present in wine, which affect the quinhydrone response of the sensor. If now DL-malic acid is dissolved in wine titrated to EP the titration curve approaches the titration curve of the wine (cf. Fig. 1). Consequently the matrix of the standard solutions used to calibrate the FIA system has to be similar to the wine matrix. To simulate the matrix of wine a solution of 4 mol L^{-1} sodium hydroxide was added successively to a wine until the pH of the wine was equal to the pH of its EP (pH ~ 7.5). This wine titrated to the EP was used as solvent for all calibration solutions and as solvent for the dilution of all wine samples.

3.2.2. Calibration curves

Calibration curves were recorded with solutions of DL-malic acid in a concentration range from 5×10^{-4} to 1.25×10^{-2} mol L^{-1}. This range corresponds to hydronium ion concentrations between 1×10^{-3} and 2.55×10^{-2} mol L^{-1}, because DL-malic acid is a dibasic acid. As solvent, white wines as well as red wines titrated to the EP were used. Asymmetric peak shaped signals, which are typical for FIA titrations, were recorded (cf. Fig. 2). The peak area (A_P) was used for calibration. With both solvents comparable calibration curves were obtained (cf. Fig. 3): linear dependences of A_P on the hydronium ion concentration were observed.

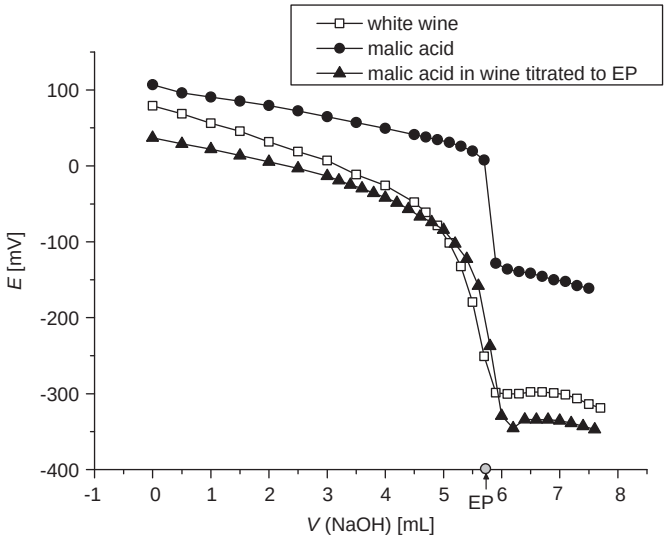

Fig. 1. Dependence of the redox potential E versus Ag/AgCl (3 M KCl) on the volume of 0.1 mol L^{-1} NaOH added to (a) aqueous solution of DL-malic acid, (b) DL-malic acid dissolved in wine titrated to EP and (c) wine.

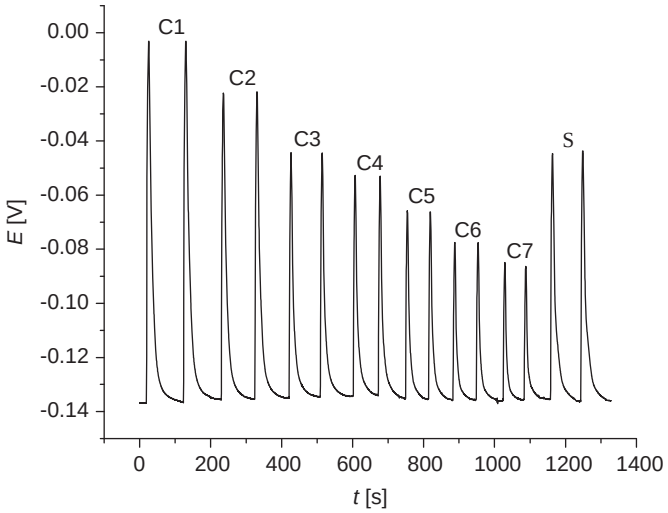

Fig. 2. Potentiometric peaks obtained for calibration solutions (C1–C7) and wine sample solutions (S) injected into the carrier solution (5×10^{-3} M NaOH + 1×10^{-2} M KCl). C1: 1.25×10^{-2} M DL-malic acid, C2: 8.75×10^{-3} M DL-malic acid, C3: 5×10^{-3} M DL-malic acid, C4: 3.75×10^{-3} M DL-malic acid, C5: 2.5×10^{-3} M DL-malic acid, C6: 1.25×10^{-3} M DL-malic acid, C7: 5×10^{-4} M DL-malic acid.

3.3. Determination of the titratable acidity of wine samples

After purging with nitrogen, the wine samples were diluted by a factor of five in a volume flask using the same white wine titrated to the EP as solvent as for the calibration solutions. The diluted wine solutions were injected into the FIA system, and the hydronium ion concentration was calculated using the calibration equation and taking into account the dilution of the wine. Eq. (1) (cf. chapter 3.1.1) was applied to calculate the titratable acidity expressed as g L^{-1} tartaric acid. In Table 2 the results of FIA titration and batch titration until the real equivalence point for different wine samples are compared.

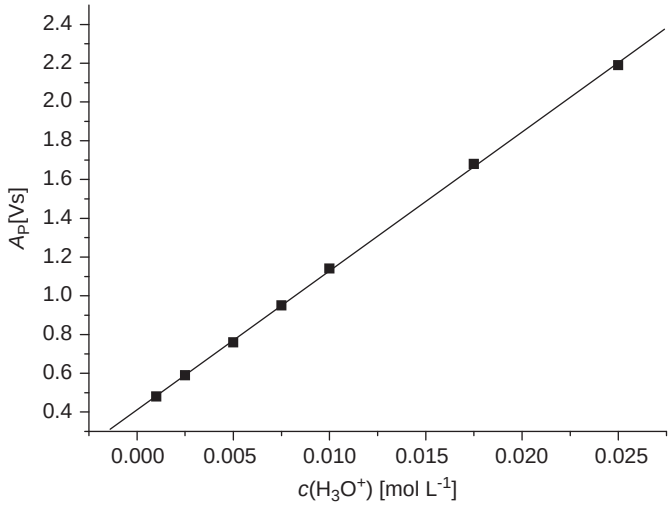

Fig. 3. Dependence of peak area (A_P) on the concentration of hydronium ions in the solution. White wine adjusted to pH 7.5 was used as solvent.

Table 2
Comparison of the results of different wine samples obtained with FIA titrations and batch titrations until the real equivalence point (number of replication is 3).

	Titratable acidity in mmol L^{-1} H_3O^+ (and in brackets in g L^{-1} tartaric acid)	
	FIA	**Batch**
red wine 1	64.8 (4.86)	68.0 (5.10)
red wine 2	63.6 (4.77)	63.3 (4.75)
red wine 3	73.3 (5.50)	73.8 (5.54)
red wine 4	75.9 (5.70)	74.2 (5.57)
white wine 1	67.5 (5.07)	65.7 (4.93)
white wine 2	68.9 (5.17)	67.8 (5.09)
white wine 3	83.3 (6.25)	82.8 (6.21)
white wine 4	79.6 (5.97)	81.5 (6.12)
rosé wine	66.6 (5.00)	63.1 (4.74)

The results of FIA titrations are in good agreement with the results obtained with batch titrations until the equivalence point. By applying a paired *t*–test it could be confirmed that for the different wine samples the titratable acidity determined with FIA titration and batch titration to the equivalence point do not differ significantly ($p=0.98$). Furthermore, the *Organisation Internationale de la Vigne et du Vin* (OIV) requires a reproducibility of 0.3 g L^{-1} tartaric acid for white and rosé wines and a reproducibility of 0.4 g L^{-1} tartaric acid for red wines [2]. That means that the differences of the results obtained with FIA titration and batch titration until the real equivalence point lie within the specified range for all the wine samples.

However, the legal requirements in the US and Europe require titrations up to pH 8.2 and 7.0, respectively; thus the results obtained by FIA titration have to be corrected. Therefore, a solution of DL-malic acid dissolved in white wine titrated to the EP was titrated with NaOH and the pH was measured after each NaOH addition. The consumption of NaOH up to pH 7 and up to pH 8.2 was determined and compared to the NaOH consumption until the real equivalence point, respectively. With respect to the NaOH addition until the real equivalence point, the added NaOH volume amounts to 96.2% in case of titration up to pH 7 and 100.5% in case of titration up to pH 8.2. These correction factors were applied to the FIA titration by multiplying the malic acid concentrations of the calibration curves with 0.962 or 1.005 to determine the titratable acidity of wine samples up to pH 7 or up to pH 8.2, respectively. In Table 3 the titratable acidity of the wine samples determined by correction of the FIA results and determined by batch titration up to pH 7 and pH 8.2 respectively are compared.

By introduction the correction values, the FIA results are in good accordance with the results of batch titration up to pH 7 and pH 8.2. The differences lie within the range specified by the OIV for nearly all wine samples. Only in case of the titration of red wine 1 up to pH 8.2 and the titration of rosé wine up to pH 7, the differences of the results determined with FIA and batch titration lie outside the required range. While the obtained deviation for the rosé wine lies only marginally outside the required range (0.33 g L^{-1}, while only a difference of 0.3 g L^{-1} is allowed), the deviation for red wine 1 is larger; here, the values determined with FIA titration and batch titration up to pH 8.2 differ by around 0.52 g L^{-1} tartaric acid, while only a difference of 0.4 g L^{-1} is allowed according to the requirements of the OIV.

Furthermore, the repeatability of the determination of titratable acidity of wine with FIA titrations was studied using a red wine. Four samples of the wine were prepared by diluting the wine using a white wine titrated to the EP as solvent. Each sample was injected in the FIA system three times and the titratable acidity was determined (cf. Table 4). Using the mean values of the four samples the titratable acidity of the studied red wine was determined to be 0.0681 ± 0.0009 mol $L^{-1}H_3O^+$ (5.11 ± 0.07 g L^{-1} tartaric acid), i.e. the standard deviation for the determination of titratable acidity of wine via FIA titration is less than 1.5%. The obtained deviation fulfils the requirements of the OIV, which asks for a repeatability of 0.07 g tartaric acid L^{-1} [2].

3.4. pH measurement

The pH values of different wine samples were measured under FIA conditions, and the data were compared with pH measurements using a conventional glass electrode. The FIA system was calibrated using Britton–Robinson buffer solutions in the pH range 2 to 8. Peak shaped signals typical for FIA were obtained and the peak height ΔE_P was used for calibration. By plotting ΔE_P versus the pH of the injected buffer solution a linear dependence with a satisfactory slope of -51.1 mV·$(pH)^{-1}$ was observed in a pH range of 2 to 6 (cf. Fig. 4). The obtained slope is smaller than the theoretical value of -59.2 mV·$(pH)^{-1}$, because the measurement requirements like small sample volume and rapid determination allowed no steady state signals. In more alkaline regions the pH dependence of ΔE_P deviates from the linear behaviour [25]. However, the linear part of the calibration curve can be used for evaluation, because the pH value of wine usually ranges between 2.9 and 4.2 [1].

Table 3
Comparison of the results of different wine samples obtained with FIA titration after multiplication with a correction factor and batch titrations up to pH 7 and pH 8 (number of replication is 3).

	Titratable acidity in mmol L^{-1} H_3O^+ (and in brackets in g L^{-1} tartaric acid)			
	Titration to pH 7		**Titration to pH 8.2**	
	FIA	**Batch**	**FIA**	**Batch**
red wine 1	62.2 (4.67)	66.2 (4.97)	65.0 (4.88)	72.0 (5.40)
red wine 2	61.1 (4.59)	62.6 (4.70)	63.8 (4.79)	67.4 (5.06)
red wine 3	70.6 (5.30)	69.7 (5.23)	73.7 (5.53)	75.9 (5.70)
red wine 4	72.8 (5.46)	71.9 (5.40)	76.2 (5.72)	75.8 (5.69)
white wine 1	64.8 (4.86)	63.9 (4.80)	67.8 (5.09)	67.6 (5.07)
white wine 2	66.2 (4.97)	65.1 (4.89)	69.1 (5.19)	69.1 (5.19)
white wine 3	79.9 (6.00)	78.5 (5.89)	83.6 (6.27)	83.2 (6.24)
white wine 4	76.4 (5.73)	78.9 (5.92)	80.0 (6.00)	82.6 (6.20)
rosé wine	63.9 (4.80)	59.6 (4.47)	66.9 (5.02)	63.9 (4.80)

Table 4
Investigation of the repeatability of the determination of the titratable acidity by FIA titration. Four samples of one wine were prepared and injected three times.

	Titratable acidity in mmol L^{-1} (in g L^{-1} tartaric acid)			
	Injection 1	**Injection 2**	**Injection 3**	**Mean**
Sample 1	67.9 (5.10)	66.9 (5.02)	67.5 (5.07)	**67.4** (**5.06**)
Sample 2	70.7 (5.31)	70.4 (5.28)	66.2 (4.97)	**69.1** (**5.19**)
Sample 3	66.0 (4.95)	68.3 (5.13)	–[a]	**67.2** (**5.04**)
Sample 4	67.8 (5.09)	70.4 (5.28)	68.0 (5.10)	**68.7** (**5.16**)

[a] Sample 3 could be injected only twice

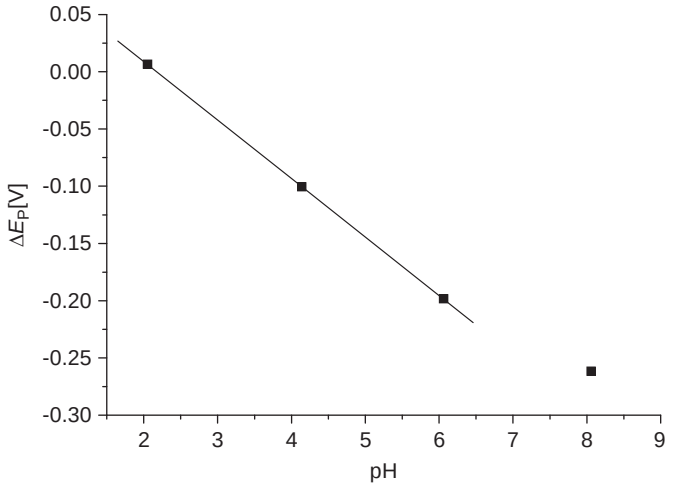

Fig. 4. Dependence of peak height (ΔE_P) on the pH of the Britton–Robinson buffer solution.

After injection of the calibration buffers, the samples were injected in the FIA system without any pretreatment, and ΔE_P was determined. The pH values of the wine samples were determined using the calibration data. Table 5 shows that there is a good agreement between the FIA measurements and the batch determinations using a glass electrode (no statistically difference, paired *t*–test, $p=0.98$). The standard deviation of the pH values of the wines determined with the FIA system is less than 1% for most of the tested wines. According to the OIV a determination within ± 0.05 pH units is necessary, so that the repeatability obtained with the FIA system fulfils also that requirement of the OIV. [2]

3.5. Determination of the sum of calcium and magnesium ions

In addition, the sum of calcium and magnesium ions in different wine samples was determined using the FIA system based on a previous study, in which we developed a method to determine calcium and magnesium ions in aqueous solutions [21]. Here, the release of protons according to the reaction of EDTA with calcium and magnesium ions and hence the change of pH in the solution is responsible for the peak shaped signals. In some cases, the amount of calcium and magnesium can also influence the quality of wine because of possible precipitation of sparingly soluble calcium salts [26,27]. In contrast to the procedure described in [21], white wine titrated to the EP as solvent was used for all calibration solutions and wine samples. The wine samples were diluted by a factor of five. Apart from that, the measurement procedure was similar to the method described in [21]. For the sake of comparison, inductively coupled plasma atom emission spectroscopy (ICP-OES) (Optima 2100 DV, Perkin Elmer, USA) was applied to determine the content of calcium and magnesium ions in the wine samples. Before the ICP-OES measurements, the wine samples have to be digested with a standard microwave digestion procedure. As can be seen in Table 6, the results obtained by FIA titration and ICP-OES measurements are in the same order of magnitude. The observed deviations could be caused by different factors, e.g. the digestion procedure. Further investigations to obtain more comparable results are underway.

Table 5
Comparison of the pH values of different wine samples determined with the FIA system and the glass electrode (number of replication is 3).

	pH	
	FIA	**Glass electrode**
Red wine 1	3.32 ± 0.01	3.32
Red wine 2	3.58 ± 0.04	3.55
Red wine 3	3.71 ± 0.03	3.73
White wine 1	3.26 ± 0.01	3.34
White wine 2	3.23 ± 0.02	3.17

Table 6
Comparison of the sum of calcium and magnesium ions of different wine samples determined with the FIA system and ICP-OES measurements.

	Sum of calcium and magnesium ions in mg L^{-1}	
	FIA	**ICP-OES**
Red wine 1	169.8	136.5
Red wine 2	132.8	165.6
Red wine 3	136.7	150.6
White wine 1	184.7	139.4
White wine 2	181.9	146.5

4. Conclusions

The present study proves that the flow injection system in conjunction with the potentiometric detector based on a quinhydrone composite electrode, as developed previously in our laboratory, is also applicable for a simple, rapid and automated determination of the acid content, the pH and the calcium and magnesium content of wine in small sample volumes.

For routine applications it is possible that the company providing the titration system will also provide wine samples which were titrated to the equivalence point, to be used for calibration. Such titrated wine samples are stable when deaerated and stored in closed bottles.

Since the legal requirements in the US and Europe require titrations up to pH 8.2 and 7.0, respectively, the results of our titration method have to be corrected by multiplication with a factor as described in this paper.

The present study also shows that in principle with the same experimental setup the determination of the sum of calcium and magnesium content is detectable.

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References

[1] J. Robinson, Das Oxford Weinlexikon, Hallwag, Bern, 1995.
[2] OIV, Compendium of International Methods of Wine and Must Analysis, International Organisation of Vine and Wine, Paris, 2011.

[3] B.W. Zoecklein, K.C. Fugelsang, B.H. Gump, F.S. Nury, Wine Analysis and Production, Chapman & Hall, New York, 1995.
[4] C.S. Ough, M.A. Amerine, Methods for Analysis of Must and Wines, second ed., John Wiley & Sons, New York, 1988.
[5] O.Y. Berezin, Y.I. Tur'Yan, I. Kuselman, A. Shenhar, Talanta 42 (1995) 507–517.
[6] E.A. Zakharova, M.L. Moskaleva, Y.A. Akeneev, E.S. Moiseeva, G.B. Slepchenko, N.P. Pikula, Russ. J. Anal. Chem. 66 (2011) 848–853.
[7] M.A. Baldo, S. Daniele, G.A. Mazzocchin, Anal. Chim. Acta 272 (1993) 151–159.
[8] S. Ohtsuki, N. Kunimatsu, K. Takamura, F. Kusu, Electroanalysis 13 (2001) 404–407.
[9] A.R. Tôrres, W. da Silva Lyra, S.I.E. de Andrade, R.A.N. Andrade, E.C. da Silva, M.C.U. Araújo, E. da Nóbrega Gaião, Talanta 84 (2011) 601–606.
[10] M. Peris-Tortajada, A. Maquieira, R. Puchades, Am. J. Enol. Vitic. 44 (1993) 118–120.
[11] R.S. Honorato, M.C.U. Araújo, R.A.C. Lima, E.A.G. Zagatto, R.A.S. Lapa J.L.F. Costa Lima, Anal. Chim. Acta 396 (1999) 91–97.
[12] A.J.C. Garcia, B.F. Reis, J. Autom. Methods Manage. Chem. 2006 (2006) 83247.
[13] E. Mataix, M.D.L. de Castro, Anal. Chim. Acta 381 (1999) 23–28.
[14] J. Marcos, A. Ríos, M. Valcárcel, Anal. Chim. Acta 261 (1992) 489–494.
[15] E.N. Gaião, R.S. Honorato, S.R.B. Santos, M.C.U. Araújo, Analyst 124 (1999) 1727–1730.
[16] T.J. Cardwell, R.W. Cattrall, G.J. Cross, G.R. O'Connell, J.D. Petty, G.R. Scollary, Analyst 116 (1991) 1051–1054.
[17] A.O.S.S. Rangel, I.V. Tóth, Analyst 123 (1998) 661–664.
[18] H. Kahlert, J.R. Pörksen, J. Behnert, F. Scholz, Anal. Bioanal. Chem. 382 (2005) 1981–1986.
[19] M. Lovrić, Š. Komorsky-Lovrić, H. Kahlert, F. Scholz, Anal. Chim. Acta 602 (2007) 75–81.
[20] K. Vahl, H. Kahlert, D. Böttcher, R. Wardenga, Š. Komorsky-Lovrić, U. Bornscheuer, F. Scholz, Anal. Chim. Acta 610 (2008) 44–49.
[21] K. Vahl, H. Kahlert, F. Scholz, Electroanalysis 22 (2010) 2172–2178.
[22] J. Růžička, E.H. Hansen, Flow Injection Analysis, second ed., Wiley, New York, 1988.
[23] H. Kahlert, J.R. Pörksen, I. Isildak, M. Andac, M. Yolcu, J. Behnert, F. Scholz, Electroanalysis 17 (2005) 1085–1090.
[24] A. Ruland, Küster-Thiel Rechentafeln für die chemische Analytik, 103rd ed., Walter de Gruyter, Berlin, 1985.
[25] H. Kahlert, in: F. Scholz (Ed.), Electroanalytical Methods: Guide to Experiments and Applications, second ed., Springer, Berlin, Heidelberg, 2010, pp. 237–256.
[26] G. Schwedt, A. Schweizer, G. Hendrich, Z. Lebensm. Unters. Forsch. 187 (1988) 229–234.
[27] D.G. Themelis, P.D. Tzanavaras, A.V. Trellopoulos, M.C. Sofoniou, J. Agric. Food Chem. 49 (2001) 5152–5155.