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Getränkeherstellung

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Getränkeanalytik

Instruction for the electrometric determination

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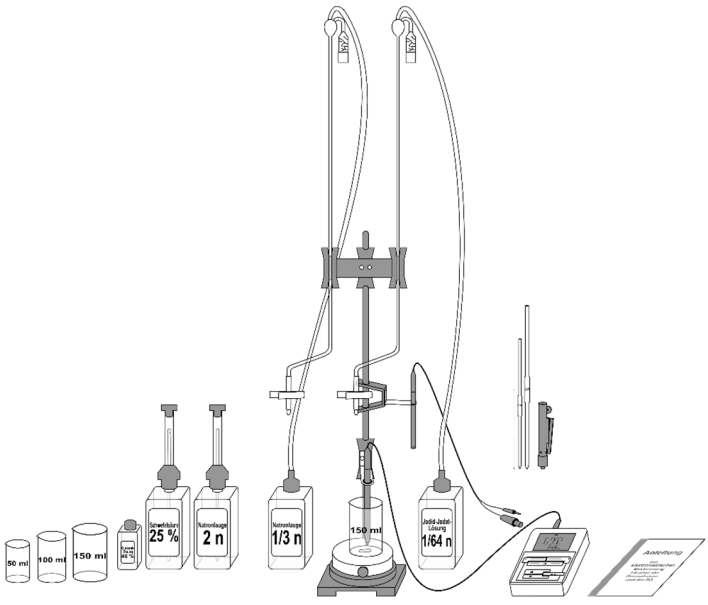
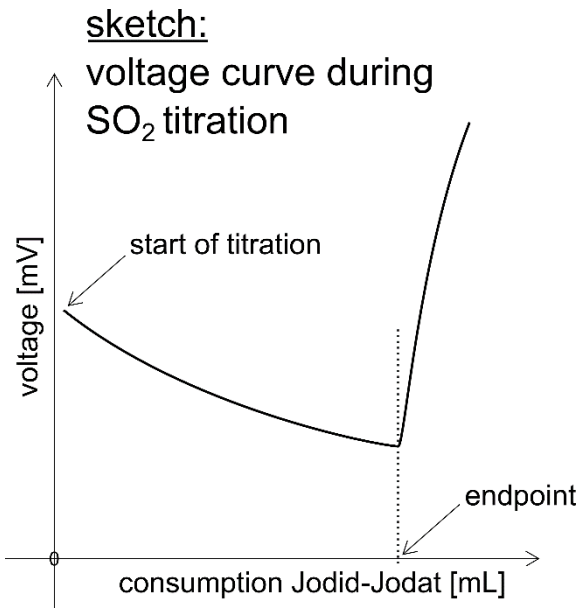
- **of the pH value**
- **of the total acidity**
- **of the free sulphurous acid**
- **of the total amount of sulphurous acid**
- **of the reductones (ascorbic acid, phenols)**





1. Determination of the pH-value:

The manufacturer's user manual is giving general notes for measuring the pH-value.
PH-electrodes change their measuring behavior over their lifetime. Therefore the pH-meter with connected pH-electrode should be regularly calibrated before starting the measurements. To do so, the buffer solutions pH 7.0 (green) and pH 4.0 (red) are required. The temperature of the buffer solutions has to be taken into account since it substantially influences the measurement. The reference temperature is 20°C.
To increase the measuring accuracy, it is recommended to swivel the pH-electrode gently during calibration in the buffer solution or to stir the solution.

Analysis procedure
Immerse the calibrated pH-electrode into the must, wine or fruit juice under the same conditions as during calibration, i.e. with waving or stirring. The pH-meter has to be in the pH-mode. The measured value can be read directly from the display. The temperature of the liquid to be examined should be around 20°C.
The use of a simple pH-meter requires the separate temperature measurement of the liquid sample and to enter the °C into the pH-meter. Using a pH-electrode with integrated temperature sensor connected to a pH-meter with automatic temperature compensation will already show the corrected pH-value.

2. Determination of the titratable total acidity:

Sample preparation
The "titratable total acidity" in wines, musts, fruit and berry juices includes by definition the organic acids tartaric, malic, lactic and citric acid. Carbonic acid perhaps present in the sample has to be removed before titration by:

- shaking the cold sample under reduced pressure (100 mL sample in a 500 mL or 1 L suction flask under vacuum of water flow pump) until no gas evolves or
- heating of the previously exactly measured volume of the sample until beginning of boiling, degassing in an ultrasonic bath and following cooling to about 20°C.

Analysis procedure

- Pipette by means of a full pipette 25.0 mL of the sample into a beaker glass, insert a magnetic stirring rod and place the beaker glass onto the magnetic stirrer.
- Immerse the pH-electrode (connected to the pH-meter switched on pH-mode) in such a way that the rotating stirring rod cannot damage the tip of the electrode. Switch-on the stirrer.
- Add slowly caustic soda solution 1/3n (sodium lye / Natronlauge 1/3n) from the 20 mL-Automatikus burette until the display will show pH 7.0 for wines (pH 8.1 for fruit juices acc. to IFU-method No. 3). This is the endpoint of the titration.
- Read the consumption of sodium lye from the burette.

Calculation and example
The "titratable total acidity" corresponds to the consumption of sodium lye 1/3n:

Titratable total acidity [g/L of sample] = Consumption of sodium lye 1/3n [mL]

Example: If for achieving the end point of titration (pH 7.0) for example 10.5 ml caustic soda solution have been used, the sample contains 10.5 g / litre of total acidity, expressed as tartaric acid.
Table XIII in the book "Aktuelle Weinanalytik" (p.116 in the 3rd edition of 2005) from our publishing house allows the conversion of this result into malic, lactic, citric or sulfuric acid.

Note for samples with very high titratable acidity (>20 g/L)
If the burette graduation is not sufficient for the titration (e.g. mother syrup from black currants), the consumed quantity of sodium lye is recorded, the burette refilled and the titration continued. The final result will be the sum of both of the found values.

3. Determination of the sulphurous acid (SO_2) and the reductones (ascorbic acid, phenols) using the pH-meter set on mV-mode and connected with the redox-electrode ORP:

General notes

-Sulphurous acid is known to react with many wine born substances and oxygen in equilibria. These reactions need time, in red wines up to three weeks. This phenomen may –despite correct analysis- cause differing results for sulphurous acid in samples of the same wine, which have been took or stored under different conditions, f.e. too early after an addition of suphur to the wine, under the influence of light or oxygen in the head space of the bottle and so on.

-The present method will be disturbed by reductones as all methods determining sulphurous acid by means of an iodometric titration. This has to be took into account in beverages with (added) ascorbic acid as well as in dark coloured juices and red wines with naturally high contents of reducing phenols.

-The iodometric titration with visual determination of the end point (change in colour) will give reliable results in white or rosé wines and in pomace fruit wines. The electrometric determination additionally will give reliable results in dark wines from red grapes, berries and stone fruits, where the change in colour is not visible.

-All methods for the determination of total sulphurous acid including an alkaline hydrolysis of the bound sulphurous acid may show results, which are a little lower than the real results, which are found after hydrolysis by heat according to the official methods. For this reason accurate determinations of the total sulphurous acid in the near of the legal limits should be done with our method "***Distillation of the total sulphurous acid according to Dr. Rebelein".***

Preparation of the pH-meter and the redox-electrode ORP

The manufacturer's user manual shows general notes for the use of the redox-electrode ORP (for measurements blue closure opened, „I"; refilled with and stored in a solution of 3m KCl, free of silver-ions). A calibration is not necessary. Of course the electrode should be thoroughly rinsed with distilled water after every use. Over night and for a longer time of not using the blue closure has to be set to "0".

For the determination of the free and total sulphurous acid as well as of the reductones, the redox-electrode ORP has to be connected to the DIN-socket of the pH-meter (instead of the pH-electrode). Then switch on the pH-meter and set it to "mV".

Sample preparation

Carbonic acid perhaps present in the sample may not be removed as this would cause losses of sulphurous acid. If bubbling avoids the accurate use of a pipette, please measure the volume as accurate as possible by using a measuring flask or a measuring cylinder. In general determinations of sulphurous acid should be achieved at around 20°C and as rapid as possible.

Analysis procedures

3. a) Determination of the „apparent" free sulphurous acid (including reductones):

- Pipette 50.0 mL of sample by means of the full-pipette into the 150mL-beaker glass. Hold the tip of the pipette closely above the bottom.
- Add 10 mL of 25% sulphurous acid by means of the dosing cylinder and insert the magnetic stirring rod into the beaker glass.
- Place the beaker glass onto the magnetic stirrer, immerse the redox-electrode ORP and start stirring.
- At once start the titration with 1/64n iodide-iodate-solution **without waiting for a constant voltage**. Please look permanently onto the display of the pH-meter. To avoid too big fluctuations the solution should not immerse too close to the electrode. You will obtain best results by adding around 3-4 drops per second (= 5-7 sec/mL).
- During the titration the voltage will decrease slowly for about 10-50 mV, than it will increase very suddenly for at least 50-100 mV.
- The sketch in the figure on page 1 is showing the end point of the titration.
- Read the consumption of 1/64n iodide-iodate-solution from the burette.

The content of "apparent" free sulphurous acid (including reductones) has to be calculated by means of the following formula:

"Apparent" free sulphurous acid [mgSO_2/L] = Consumption of iodide-iodate-solution [mL] x 10

3. b) Determination of the „real“ free sulphurous acid (without reductones):

For the determination of the “real” free sulphurous acid, at first the “apparent” free sulphurous acid including reductones has to be determined according to the instructions ***3.a)***. In a second step, the free sulphurous acid contained in a sample of the same beverage is bound by adding glyoxal solution; then the determination has to be carried out once again, so that the result will be the content of reductones. Finally the calculated difference between both results will give the “real” free sulphurous acid.

- Pipette 50.0 mL of wine into the 150ml-beaker glass.
- Add 40% glyoxal solution by means of a 2 ml volumetric pipette or a dosing cylinder and swivel gently.
- Add approx. 5 minutes later (in this period, the free sulphurous acid will be bound) 10 mL of 25% sulphurous acid by means of the dosing cylinder and insert the magnetic stirring rod into the beaker.
- Place the beaker onto the magnetic stirrer, immerse the redox-electrode ORP, start stirring and achieve the titration as described in the frame in chapter ***3.a)***.

The following formula will give the content of reductones, expressed as apparent sulphurous acid:

Reductones [mg SO_2 / L] = Consumption of iodide-iodate-solution [mL] x 10

The difference between the burette readings of both titrations (without/with glyoxal) will give the “real” free sulphurous acid:

“Real” free sulphurous acid [mg SO_2 / L] = Difference between titration results [mL] x 10

Use the following formula for expressing the reductones as ascorbic acid (2,75 is the factor between the molecular weights of ascorbic acid and SO_2):

Reductones [mg ascorbic acid/L] = Reductones [mg SO_2/L] x 2,75

3. c) Determination of the total sulphurous acid including reductones by alkaline hydrolysis:

- Pour 10 mL of 2n sodium lye into the 150mL-beaker glas by means of a dosing cylinder.
- Add 50.0 mL of wine using the full-pipette (immerse the tip of the pipette a bit into the liquid).
- Mix the content of the beaker-glass by gentle swiveling and let it stand for 5 minutes (hydrolysis).
- Add 10 mL of 25% sulphurous acid (dosing cylinder) and insert the magnetic stirring rod into the beaker.
- Place the beaker onto the magnetic stirrer, immerse the redox-electrode ORP, start stirring and achieve the titration as described in the frame in chapter ***3.a)***.

Calculate the content of the total sulphurous acid (including reductones) by means of the following formula:

Total sulphurous acid [mg SO_2 / L] = Consumption of iodide-iodate solution [ml] x 10

Additional important notes:

- If the burette graduation is not sufficient for the titration, record the measured value, refill the burette and continue the titration. Then calculate the sum of both consumptions of iodide-iodate.
- To diminuish the total sulphurous acid including reductones by the content of reductones, it is necessary to determine their concentration according to ***3.b)*** and to deduct it from the result of procedure ***3.c)***.

4. Determination of sulphurous acid by means of 1/128n iodide-iodate solution:

Instead of 1/64 n iodide-iodate solution also a 1/128 n iodide-iodate solution can be used for the titration. In this case, only 25 mL of sample have to be used. The procedure is implemented analogue to all of the above described instructions (same volumes of reagents, same calculations).