



Basic principles of water measurement technology

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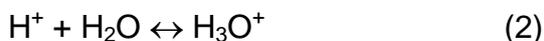
What is the pH value?

We are all familiar with the term "pH value" from advertisements for "pH-neutral skin care products" or "acid rain". However it is also an important biological quality characteristic of water. The pH value of drinking water is not only important on health grounds, it is also subject to tolerance limits used for the protection of drinking water pipelines against corrosion. Higher efficiency can also be achieved in chemical processes, plastics manufacturing and the scrubbing of exhaust air by adjustment to the correct pH value.

Aqueous solutions always contain H_3O^+ and OH^- ions. They are in equilibrium with water (H_2O). The following equations express the self-dissociation of the water.



We usually refer to hydrogen ions H^+ , although they only occur in hydrated form in aqueous solutions. Water molecules react with hydrogen ions to form hydronium or oxonium ions H_3O^+ . This is based on the following chemical equation.



The hydrogen ion thus usually occurs in the associated form.

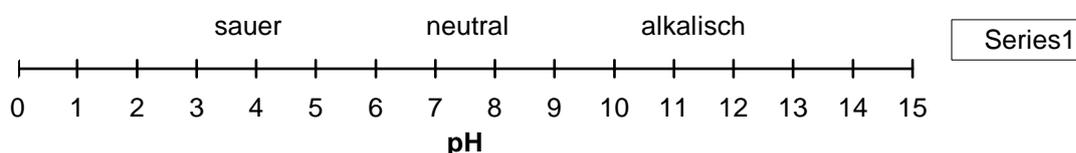
The pH value provides information on the free acid or free alkali present in a medium and has been defined by *Størensen* as the negative common logarithm of the hydrogen ion concentration $c(\text{H}^+)$.

$$\text{pH} = -\log [\text{H}^+] \quad (\text{Størensen, 1909}) \quad (3)$$

If acid ($\text{H}^+ \rightarrow$ hydrogen ion) is dominant in a solution, we refer to an acidic solution and the pH value will lie between pH 0 and pH 7. The more acidic the solution, the lower the pH value and the higher the concentration of hydrogen ions. This corresponds to *Størensen's* equation.

If alkali ($\text{OH}^- \rightarrow$ hydroxide ion) predominates, we refer to a base or alkaline solution. The pH value lies between pH 7 and pH 14. In this case, the more alkaline the solution, the higher the pH value.

pH values are measured in the range between pH 0 and pH 14. This is illustrated by the scale below.



Basic chemical principles

The law of mass action¹ can be applied to the self-dissociation of water. Thus:

$$[\text{H}_3\text{O}^+][\text{OH}^-] / [\text{H}_2\text{O}]^2 = K_C \quad (4)$$

The equilibrium is on the right-hand side and K_C has a very small numerical value. In pure water and diluted solutions the concentration of the H_2O molecules can be regarded as constant. The equation can therefore be simplified to (simplification: $[\text{H}^+]$ instead of $[\text{H}_3\text{O}^+]$, this is customary):

$$[\text{H}^+][\text{OH}^-] = K_W \quad (5)$$

where K_W represents the ion product of the water. At a temperature of 25°C this has a numerical value of $K_W = 10^{-14}$. In pure water H^+ and OH^- ions occur in equal quantities, $[\text{H}^+] = [\text{OH}^-]$, thus:

$$[\text{H}^+]^2 = 10^{-14} \text{ mol}^2/\text{L}^2 \quad (6)$$

$$[\text{H}^+] = 10^{-7} \text{ mol/L} \quad (7)$$

Logarithmic quantities are introduced to avoid having always to use powers:

$$\text{pH} = -\log [\text{H}^+] \quad (8)$$

$$\text{pOH} = -\log [\text{OH}^-] \quad (9)$$

Formulated logarithmically, the ion product of the water is now expressed as follows

$$\text{pH} + \text{pOH} = \text{p}K_W \quad (10)$$

where the negative logarithm is also used for the constant K_W : $\text{p}K_W = -\log K_W$.

If the concentration of hydrogen ions is reduced by the power of ten, the pH value increases by one unit. When the concentration of H^+ ions is increased, the pH value is reduced. Table 1 summarizes the existing H^+ and OH^- ion concentrations.

Range	pH value	$[\text{H}^+]$ in mol/L	$[\text{OH}^-]$ in mol/L
	0	1	0,00000000000001

¹ The position of a chemical equilibrium is described by the law of mass action (LMA). Equilibrium constant K_C is defined as the product of the concentration of final substances (right-hand side of the arrow) divided by the product of the concentrations of the starting substances (left-hand side of the arrow). The equilibrium constant depends only on the temperature.

For a generally formulated reaction equation $aA + bB \leftrightarrow cC + dD$

the LMA is as follows $[\text{C}]^c [\text{D}]^d / [\text{A}]^a [\text{B}]^b = K_C$

If $K \gg 1$, the reaction proceeds almost entirely in the direction of the end products.

If $K = 1$, all participants in the reaction are present in equilibrium in comparable concentrations.

If $K \ll 1$, the reaction virtually does not occur.

² mol/L: indication of chemical concentration; $1 \text{ mol} = 6 \cdot 10^{23}$ atoms, ions or molecules,
 $1 \text{ mol/L} = 6 \cdot 10^{23}$ atoms, ions or molecules / litre

	1	0,1	0,0000000000001
	2	0,01	0,000000000001
acidic	3	0,001	0,00000000001
	4	0,0001	0,0000000001
	5	0,00001	0,000000001
	6	0,000001	0,00000001
neutral	7	0,0000001	0,0000001
	8	0,00000001	0,000001
	9	0,000000001	0,00001
	10	0,0000000001	0,0001
alkaline	11	0,00000000001	0,001
	12	0,000000000001	0,01
	13	0,0000000000001	0,1
	14	0,00000000000001	1

Table 1: pH scale for solutions and concentrations up to 1 mol/l

The pH value is measured by using an electrode. The most important component of the electrode is the pH glass. This has the characteristic of generating an electrical potential as a function of the pH value. This potential is transmitted on the inside of the electrode to the measuring conductor via the measuring electrolyte (KCl). The measuring electrolyte and the glass membrane have the same pH value. Standard conductors consist of a silver wire with a silver chloride coating. (Fig. 1)

In pH measurement an electric voltage U is therefore measured, which is expressed mathematically by the Nernst equation:

$$U = U_0 + \frac{R T}{F} \cdot \log [H^+] \quad U_0 \text{ standard potential} \quad (11)$$

R gas constant
 T temperature
 F Faraday constant

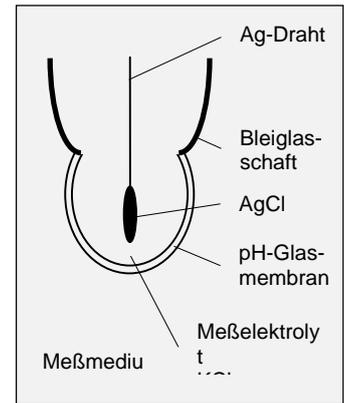


Fig. 1: pH electrode

This equation shows that the pH measurement is a function of the temperature. pH measurements are therefore often performed in conjunction with temperature compensation. Since an electric voltage is being measured, a second pole must be available against which the measurement can be made. A so-called reference electrode must therefore be connected beside the pH electrode (Fig. 2a). This reference electrode must not be influenced by the pH value. Its internal conducting system is similar to that of the pH electrode in order to obtain stable temperature behaviour and high measuring accuracy. The circuit is closed via a membrane between the medium being measured and the internal electrolyte of the reference electrode. The reference electrolyte for pH electrodes is potassium chloride (KCl).

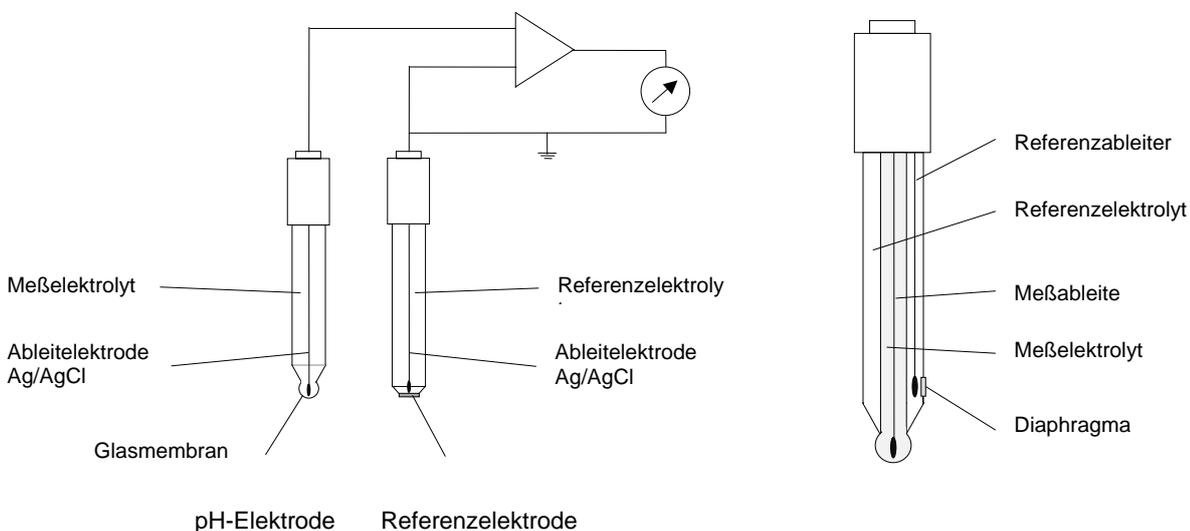


Fig. 2a: Two-part measuring chain

Fig. 2b: Combined measuring chain

The two electrodes can also be combined in one, thus creating a so-called combined measuring chain (Fig. 2b). This version is equally efficient but easier to handle and is used today in most applications.

The shank of a **combined measuring chain** is made from lead glass, since this has the same expansion properties as platinum. This is important, since leakage of measuring

electrolyte is prevented by a glass seal in the upper part of the electrode. Voltage is transferred through this glass seal by means of the platinum wire.

The glass membrane is made from special glass and consists of 21 components. It is between 150 and 250 µm thick.

The contact area between the reference electrolyte and the solution being measured, **membrane**³, is a crucial point in this measuring system. The pressure of the water must not be greater than the pressure exerted by the reference electrolyte on the membrane from inside, otherwise the solution being measured could penetrate it and the properties of the reference electrolyte would be changed. This would result in a faulty measurement. Electrodes are therefore always designed so that there is a small loss of reference electrolyte by diffusion into the solution being measured. This is regrettable, but unavoidable if correct measuring results are to be obtained. It is therefore necessary to check the level of the reference electrolyte regularly and top it up if necessary.

The membrane should always behave neutrally, not permit any diffusion, not become choked, maintain a constant discharge rate, be easy to clean and – last but not least – be small.

These are many demands on an important point in the measuring circuit, so that this function cannot be performed by one and the same membrane, depending on the application. Table 2 lists the materials used. The good properties of ceramics membranes mean that they are used in about 95% of all electrodes.

Material	Chemical influence	Physical resistance	Danger of choking	Constant discharge rate	Discharge volume	Susceptibility to contamination	Size	Price
Fibreglass	neutral	moderate	relatively high	no	uncontrollable	high	small/long	cheap
Ceramics	neutral	good	moderate	yes	provided	moderate	small	medium
HF-resistant ceramics	neutral	good	moderate	yes	provided	moderate	small	expensive
Ground glass, solid	neutral	moderate	low	yes	as required	low	large	expensive and complicated
Ground glass, opening	neutral	limited	minimal	rather no	variable	can be cleaned	large	expensive
Platinum wire	depending on sample	very good	relatively high	no	uncontrollable	low	small/long	expensive
Teflon	neutral	limited	moderate	>>>	uncontrollable	low to minimal	medium to large	complicated

Table 2: Comparison of membrane materials (guideline)

Calibrating pH electrodes

³ A membrane is a partition made from porous material.

Before an electrode is calibrated it should be placed for some time in water or KCl solution so that the glass can swell and is washed out. The calibration can be performed when this has been done.

The electrical zero point of a pH measuring chain is always at the same pH value as that of the measuring electrolyte. Measuring electrolytes with a pH value of pH 7 are therefore used in most cases. The voltage generated by a properly functioning pH measuring chain is 58 mV per pH unit. The voltage measured thus rises with increasing pH values (pH>7) and becomes negative below pH 7.

It is important in pH measurement that the electrical zero point of the measuring chain $U=0$ does not correspond to the zero point of the quantity being measured, i.e. pH 0, but is at pH 7! If the electrode is immersed in a solution with a pH value of 0, a voltage of $-58 \text{ mV} \cdot 7 = -406 \text{ mV}$ is measured. -58 mV , because it is below the zero point, and multiplied by 7, because it is 7 pH units below the zero point. Fig. 3 illustrates this.

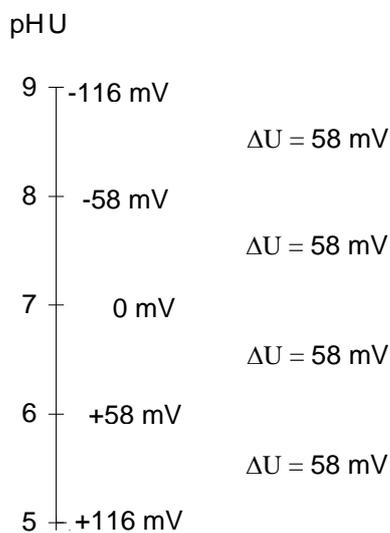


Fig. 3: mV reading as a function of the pH value

Fig. 4 gives an explanation of the calibration procedure.

The **zero point** is set by means of a buffer solution with pH 7. The calibrating line is shifted in the direction of the mV axis (Fig. 4a).

The **gradient** of the lines is then adjusted with a second buffer solution; a solution with pH 4 or pH 10 is usually used (Fig. 4b). The required measuring range is important for selecting the correct buffer solution for calibration. There should be at least 2, or preferably 3 pH units between the buffer solutions used for zero point and gradient adjustment. It is generally the case that the wider the difference in pH during calibration, the more accurately the gradient of the calibrating lines can be defined, and the more precise the measuring results will be.

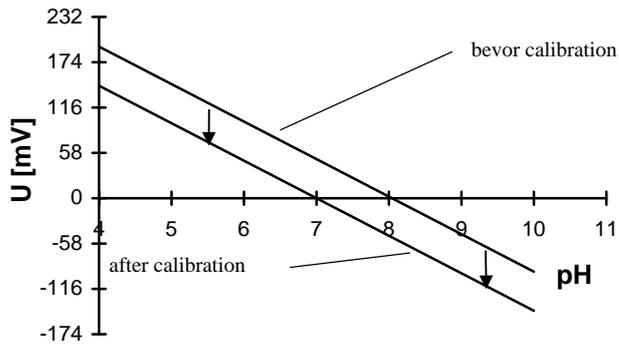


Fig. 4a: Zero point adjustment

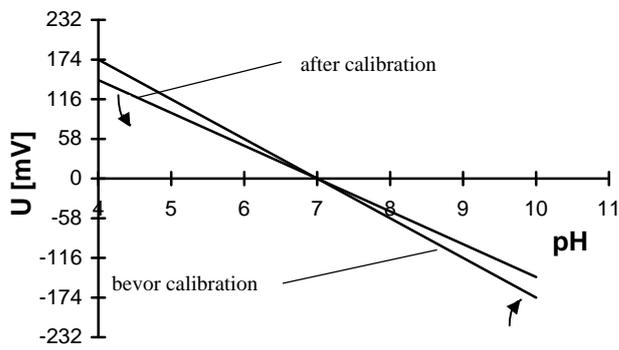


Fig. 4b: Calibration

Calibration on-site should be performed as far as possible under the same conditions, since a differential measurement is involved, i.e. it must be ensured that the same procedure is always followed in calibration.

When replacing electrodes on-site, strict care must always be taken to ensure that no water touches the plug-in contacts either of the electrode or of the plug, since this causes a short circuit and destroys the electrode (internal resistance of the electrodes in the MΩ range).

If the membrane of an electrode is contaminated, e.g. by a black coating caused by escaping silver ions which react with anions from the solution being measured (S^{2-} , Br^- , NO_3^-) to form slightly soluble silver salts, it must be cleaned with thiourea. It is best to use a cloth for this purpose and wipe the electrode from top to bottom. Rubbing the glass membrane can considerably increase the response time and should therefore be avoided. Cleaning with concentrated HNO_3 (nitric acid \Rightarrow !!wear protective gloves!!) is often sufficient to remove deposits.

If an electrode is not being used, it should be kept in 3 molar KCl solution enriched with AgCl so that the glass membrane does not dry out. After dry storage over very long periods it is advisable to reactivate the glass membrane with a hydrofluoric acid (HF) or sodium fluoride/sulphuric acid solution ($NaF + H_2SO_4$). The electrode is immersed for about one minute in the selected solution for this purpose, then rinsed and soaked for 12 hours in KCl solution.

Before inserting new electrodes, the rubber cap or plug on the lateral filler pipe for the reference electrolyte must be removed or the nipple cut off in order to ensure pressure equalization with the ambient atmosphere (so that none of the solution being measured can penetrate into the reference electrolyte! See preceding pages).

What are gel electrodes?

Gel electrodes have the same structure as "normal" electrodes. The only distinction is the different filling material of the reference electrolyte. As their name implies, the reference electrolyte in gel electrodes consists of a peptide, cyanoacrylate or cellulose-based or polymer gel. The reference electrolyte cannot be topped up in this type of electrode. Once the electrolyte is used up, the electrode must be replaced by a new one.

Many suppliers propagate gel electrodes as maintenance-free. Both of these electrode types are therefore compared below.

	"Normal" electrode	Gel electrode
pH membrane	same	same
Membrane	same	same
Internal conduction	same	same
Reference system	same	same
Cable/Connections	same	same
Opening for electrolyte	provided	not provided
Contamination risk	same	same
Physical stability	same	same
Chemical stability	same	same

Table 3: Comparison of "normal" electrodes with gel electrodes

Ion-selective electrodes

With ion-selective electrodes (ISE) it is possible to measure specific ions selectively in a solution. For this it is necessary initially to separate the ions to be detected from the others present in the solution in order then to measure them with a suitable measuring system. An ion-selective electrode is shown in Fig. 1.

The most important component of this type of electrode is the membrane, which as far as possible allows only one type of ion to pass through it. It is made of PVC and is coated with a crown ether⁴ on the side facing the solution being measured. A form selection is performed by means of this crown ether. The ions selected are held on the membrane surface by the crown ether. Depending on the ion concentration, a potential is created on the membrane surface which is transmitted to the conductor by the internal electrolytes.

As in pH measurement, this measuring system also needs a reference electrode which relates the potential measured to the electrical zero point of the solution being measured.

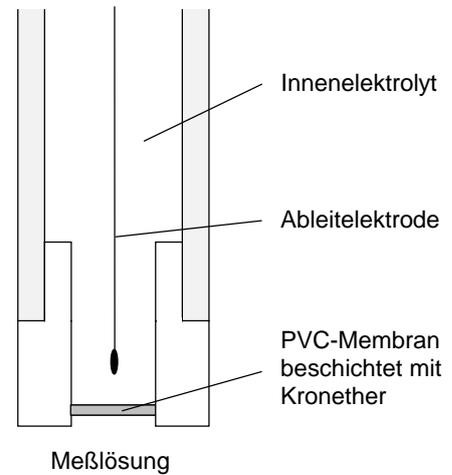


Fig. 1: Ion-selective electrode

Ion-selective measurement always involves an ion-selective electrode and a reference electrode. This is a two-part measuring chain.

The internal electrolyte should be replaced at regular intervals, but after no longer than one year.

Gas-sensitive electrodes

⁴ Crown ethers are cyclical compounds which can include other atoms, ions or molecules in their annular structures. Crown ethers can be synthesized chemically and different forms and ring sizes can be produced. The ring interstices created can be adjusted to the ion being measured by appropriate adaptation of the shape and diameter of the crown ether.

The presence in gaseous form of certain molecules, such as NH_3 , CO_2 , H_2S or NO_2 , in aqueous solutions can be determined selectively by using gas-sensitive electrodes. A gas-permeable, hydrophobic PTFE membrane is the connecting link between the solution being measured and the external electrolyte of the electrode. An ion-selective electrode is immersed in the external electrolyte. In this way the NH_3 content, for example, can be determined by measuring the pH value of the external electrolyte. In the case of gas-sensitive electrodes the external electrolyte always contains ions with which the gas being measured is in chemical equilibrium, i.e. for example NH_4^+ ions for NH_3 measurement or HCO_3^- ions for CO_2 measurement. The structure of the gas-sensitive electrode is illustrated in Fig. 1. The reference electrode surrounds the measuring electrode.

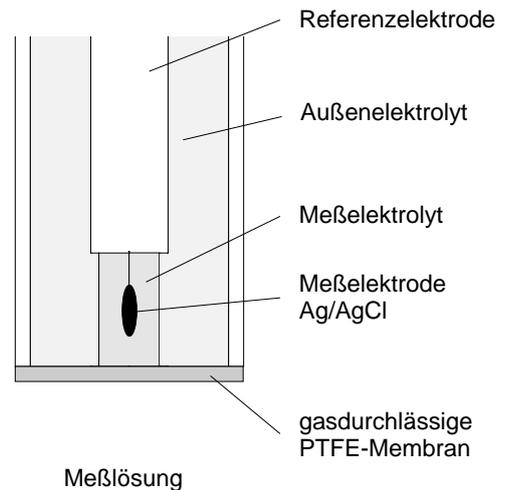
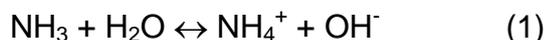


Fig. 1: Gas-sensitive electrode

If, for example, the solution being measured contains ammonia (NH_3), the gas diffuses through the microporous PTFE membrane until the partial pressure⁵ of the ammonia is the same on both sides of the membrane. The partial pressure of the ammonia is proportional to its concentration in the solution. It is thus possible to obtain information about the concentration of ammonia in the solution.

The ammonia electrode is filled with an aqueous ammonium chloride solution (is adjusted to the brine mixture in the case of special measurements in brine circuits). The ammonia diffusing in through the membrane reacts with the water of the external electrolyte and changes its value according to the equilibrium between ammonia and ammonium:



The law of mass action, which expresses the ratio of ammonia molecules to ammonium and hydroxide ions, is applicable to this balanced reaction. K is a constant.

$$[\text{NH}_4^+] [\text{OH}^-] / [\text{NH}_3] = K \quad (2)$$

The electrolyte in the electrode provides a large number of ammonium ions, so that the concentration of the ammonium can be regarded as constant, thus

$$[\text{OH}^-] = [\text{NH}_3] K' \quad (3)$$

K' is also a constant.

The measuring system behind the PTFE membrane in the electrolyte is an ISE electrode which now measures the concentration of the OH^- ions (or H^+ ions) which are generated.

⁵ Dalton's law of partial pressures states that the total pressure of a gas in mixture is equal to the sum of all partial pressures of the individual components.

$$p = p_1 + p_2 + p_3 + \dots$$

Using the law of ideal gases $pV = nRT$ can be calculated by structural change and use of the partial pressure as:

$$p_i = x_i p_{\text{ges}}$$

p_i : partial pressure of the component i

x_i : content of the component i ($x_i = n_i / n_{\text{ges}}$ with n : content in mol)

As with ion-selective measurement, the Nernst equation is also applicable here:

$$U = U_0 - R T / F \cdot \log [\text{OH}^-] \quad (4)$$

If (3) is substituted in (4), the result is

$$U = U_1 - R T / F \cdot \log [\text{NH}_3] \quad (5)$$

The voltage measured by the electrode is therefore directly proportional to the concentration of ammonia in the solution being measured.

Together with the reference electrode surrounding the glass electrode, the gas-sensitive electrode represents a combined measuring chain.

Monitoring NH₃ cryogenic circuits

Comparison of pH and gas-sensitive measurement in applications with

cryogenic circuits

The development of cooling agents has also continued parallel with the development of mechanical processes. Initially, highly toxic substances such as ammonia, methyl chloride or sulphur dioxide were used. Their toxicity, and thus the potential hazard represented by the cooling agents, encouraged the development of other, less hazardous coolants. Thus chlorofluorocarbons (CFCs) were developed and used in refrigeration equipment after 1930 in America and after 1940 in Europe. These substances display outstanding thermodynamic properties and are often non-toxic but, as research findings in the Eighties revealed, they destroy the ozone layer in the stratosphere. This resulted in restrictive regulations and prohibitions, so that ammonia is now celebrating a renaissance as a cooling agent.

First of all Fig. 1 explains the operating principle of a refrigerating plant with a compressor. These units need a compressor, which is usually electrically powered, a condenser, a diffuser (expansion valve) and a vaporizer (heat exchanger) in which the cold which is generated is transferred to a medium.

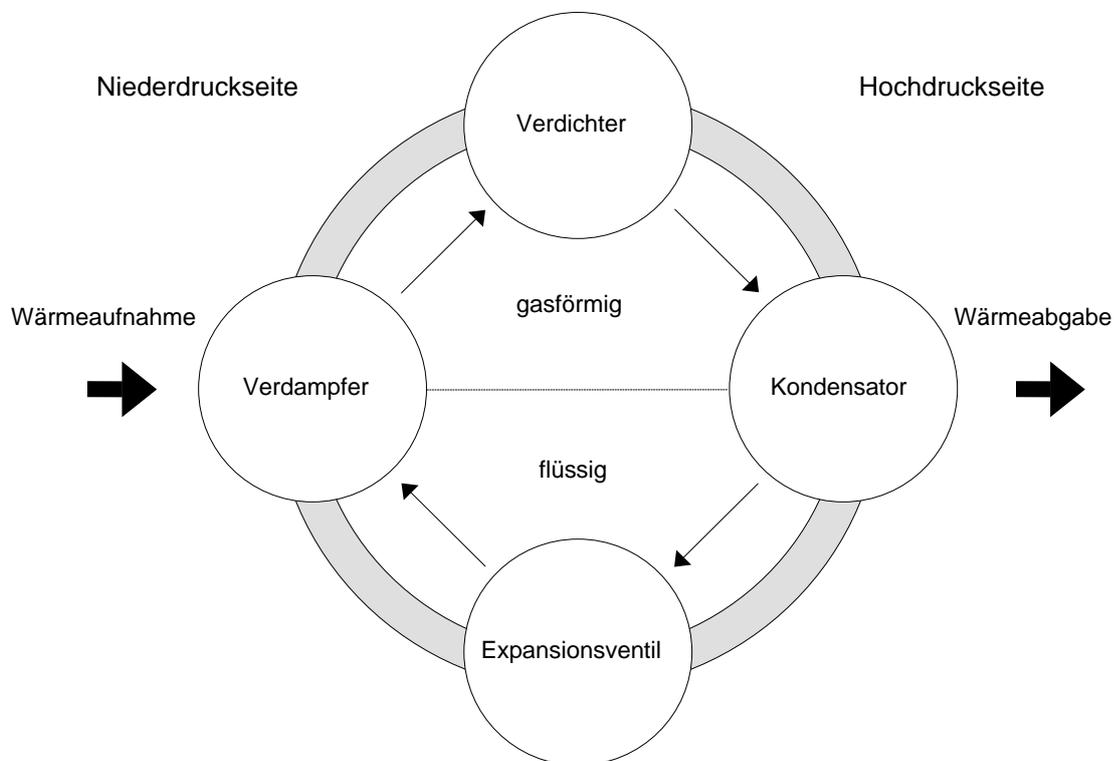


Fig. 1: Operating principle of a compressor refrigerator

The liquid coolant absorbs heat from the medium being cooled in the vaporizer and is vaporized in the process. The gas produced is compressed with a compressor, i.e. the pressure and temperature of the gas are increased. The heat generated is withdrawn from the gas in a condenser through condensation, leaving a liquid coolant under high pressure. The temperature of the coolant is reduced sharply by sudden expansion (reduction of the pressure) in the diffuser. The cycle now recommences. The heat removed in the condenser can, for example, be used to operate a heater.

When an ice skating rink is being cooled, the concrete slab under the ice is, for example, cooled directly with ammonia. The vaporizer in this case would therefore be the concrete

slab. It is obvious that large quantities of ammonia have to be used in such a process, and the potential hazard is correspondingly large. Indirect cooling processes comprising primary and secondary cryogenic circuits are therefore being used to an increasing extent. The quantity of toxic primary coolant (ammonia) can then not only be reduced drastically, the potential risk from the ammonia remains initially confined to the machinery room.

The secondary cryogenic circuit comprises one more vaporizer. The secondary coolant, e.g. brine, is cooled by the primary coolant in the first heat exchanger and now provides in turn the cold to cool another medium in the second vaporizer (using the example of the ice skating rink, this would be the concrete slab) (Fig. 2).

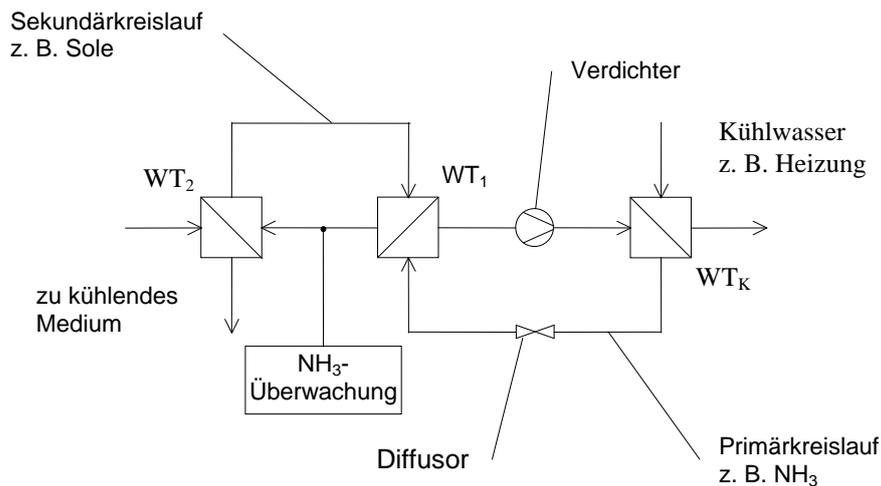


Fig. 2: Structure of an NH_3 refrigeration unit with secondary cryogenic

In addition to reducing the quantity of dangerous ammonia, the secondary circuit can take place in a copper pipe. This enhances efficiency, since improved heat transfer is achieved due to the high thermal conductivity of copper. Copper pipes are not suitable for carrying ammonia, since ammonia immediately reacts with the copper to form a stable metal-ammonia complex. The copper pipe would quickly be destroyed by even minimal leaks of NH_3 .

It is therefore not only appropriate from an economic standpoint to detect leaks of even minimal amounts of ammonia from the vaporizer into the secondary circuit in order to keep losses as small as possible; it is above all urgently necessary in order to prevent the destruction of the pipeline system by ammonia.

The logical consequence is thus to inspect the secondary circuit for an ammonia leak. If the secondary coolant is ordinary water, pH measurement can be used to a limited extent. As soon as ammonia escapes into the water due to a defect (e.g. a crack in the vaporizer), its pH value rises. However, response sensitivity even in the case of water depends on the water quality and calcium content (water hardness). When a pre-set alarm level is exceeded a warning is given, whereupon the cause of the alarm can be sought and appropriate countermeasures can be initiated.

However, if brine is used, pH measurement is of no use, since a system of this kind has the characteristic of buffering added alkaline or acidic substances. This means that

the pH value remains constant until the buffer capacity is exhausted, and only then does the pH value change.

In cooling brines there are many such buffers, e.g. potassium acetate, potassium formate, acetic acid buffer in tyfoxite, antifrogen, formic acid buffer on peka brine, etc.

If pH measurement is used, a change in pH would only occur at a concentration of several hundred up to 1000 ppm of ammonia. Much too late to protect the unit against dangerous, aggressive ammonia.

In brine circuits (such as ethylene or propylene glycol, tyfoxide, etc.) pH measurement cannot detect an ammonia leak.

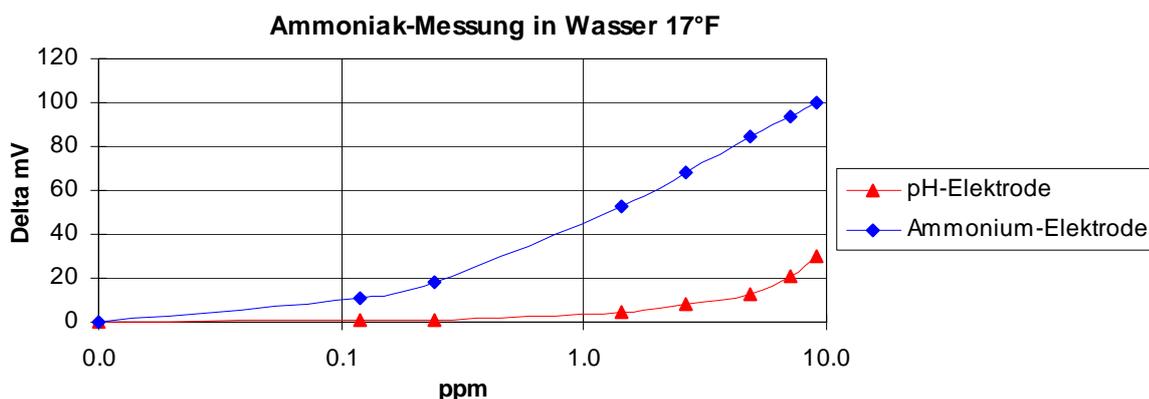
An ion-selective measuring system operating independently of pH must therefore be used in these cases.

GfG's ion-selective measuring method is an example of a measuring system of this kind.

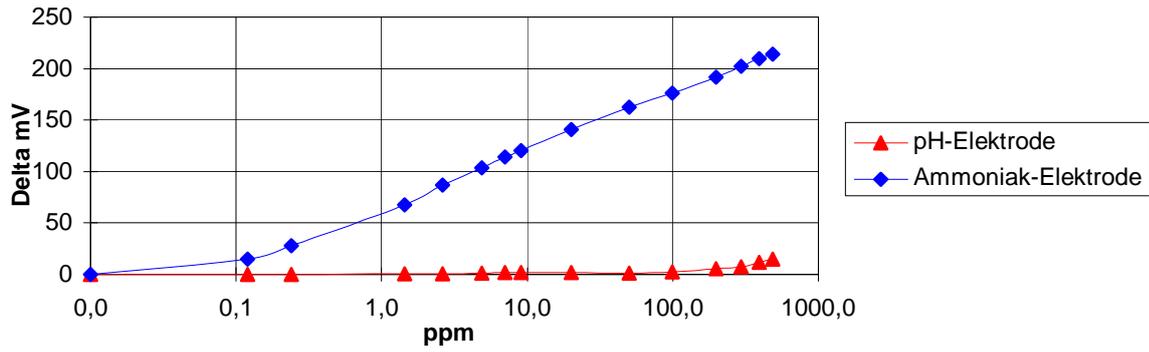
Ammonia can be detected independently of the pH value; only a few molecules are needed to obtain a reading. Concentrations of as little as 0.2 ppm can be detected with certainty, thus ensuring safe, timely warning.

The diagrams below graphically illustrate the advantages of ion-selective measurement compared with pH measurement. It is evident that ion-selective measurement displays higher sensitivity even when ordinary water is used. The tests are very easy to reproduce. Two corresponding electrodes and an evaluation unit are all that is needed. If ammonia is dripped into brine it can be seen that ion-selective measurement immediately shows a reading, whereas pH measurement shows no response.

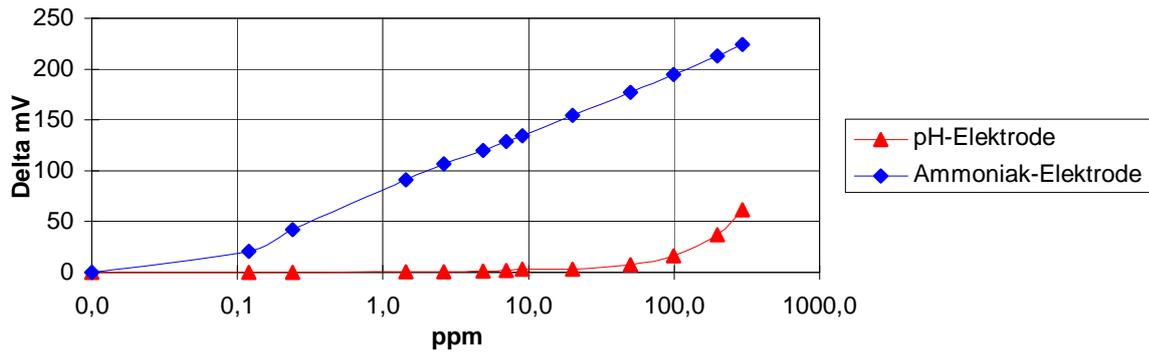
As described above, detection of minimal concentrations is extremely important !!!! Ion-selective measuring systems from GfG offer a measuring range of 0.2 ...20/40 ppm NH₃.



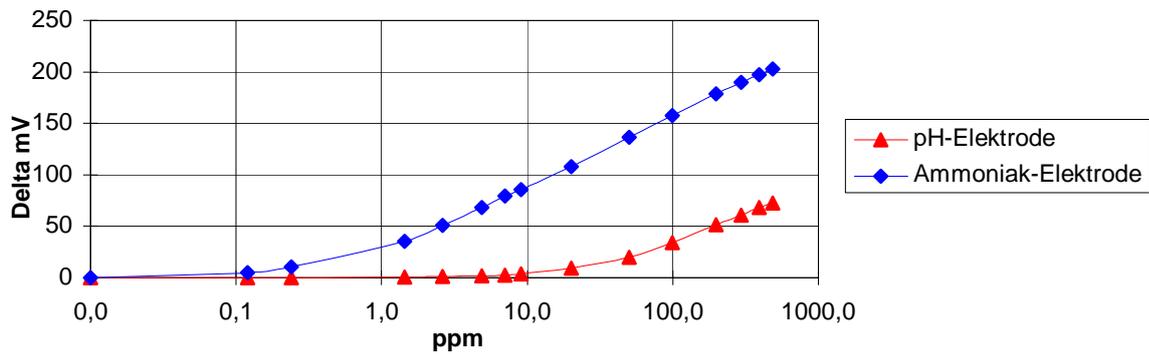
Ammoniak-Messung in Ethylenglykol 30%



Ammoniak-Messung in Propylenglykol 25%



Ammoniak-Messung in Tyfoxid 60% (Abb.5)



Ammoniak-Messung in Tyfoxid 80%

