Practice for estimating pH (ASTM D8294-21)

Rapid Tests

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MN
Since 1911

Agenda

Company

pH-testing experience

pH uncertainty

pH buffering

ASTM Practice

Summary

Company

MN Water Analysis

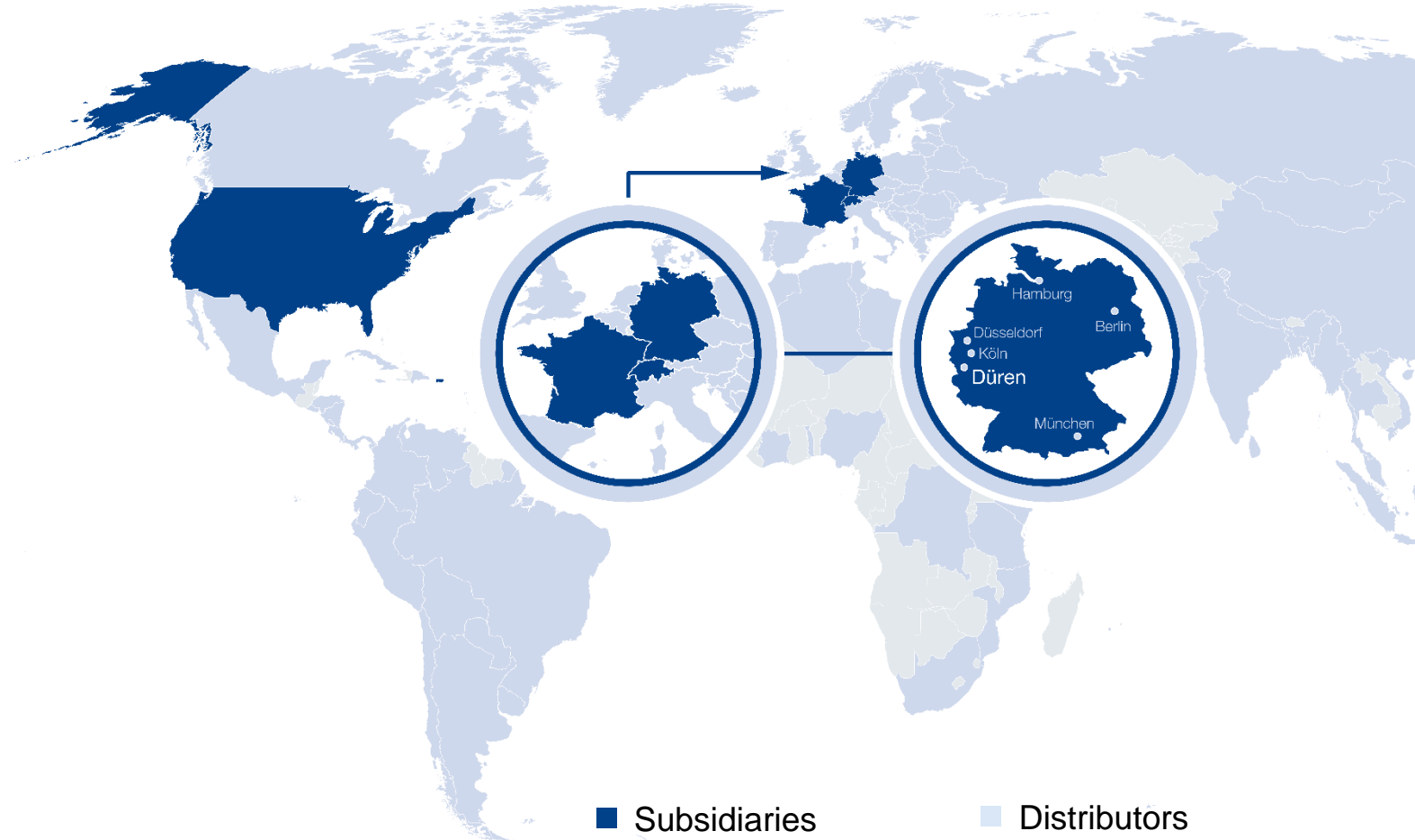# Company

MN today

- 4th Generation family owned

- More than 700 employees

- More than 25.000 products

- Turnover 120 Mio. €

Subsidiaries   Distributors

Hamburg
Düsseldorf   Berlin
Köln
Düren
München

Company

Business units

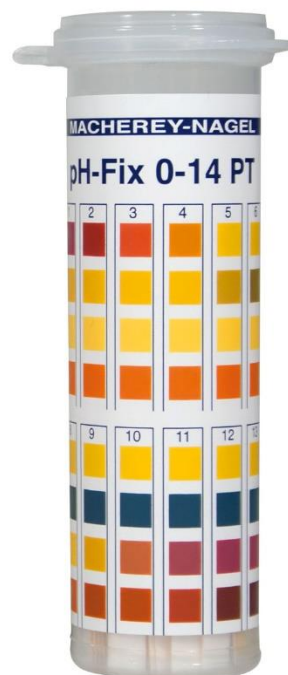| 1911	1959	1961	1970	1989
Filtration	Rapid Tests	Chromatography	Water Analysis	Bioanalysis

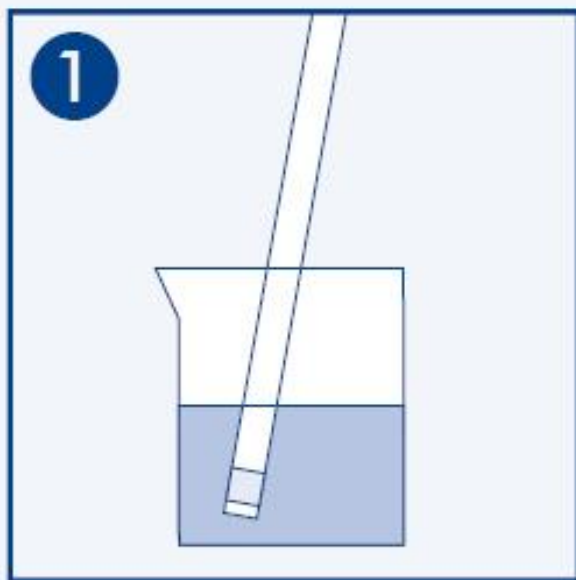# Company

pH test papers and test strips

pH testing experience

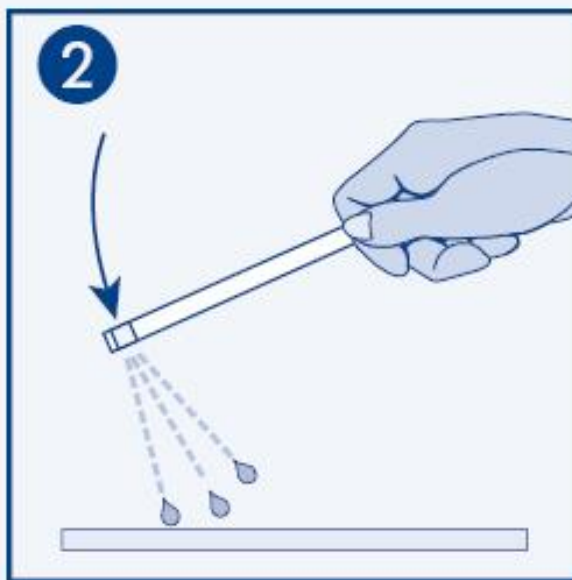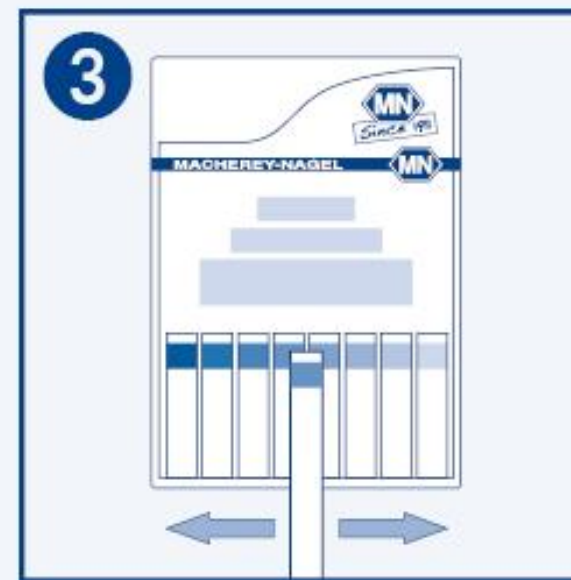# pH testing experience

Using pH-Fix test strips

1 Dip in

2 Shake off

3 Read result

pH testing experience

Why bother?

- pH is a little more complex than many people think
    - consistently underestimated factor
    - often overseen
    - sometimes counter-intuitive
- Lack of knowledge may have consequences
    - Transfer ideas where it is not appropriate
    - "interesting" decisions
    - long term practices that are simply not working
- pH testing is used in many methods
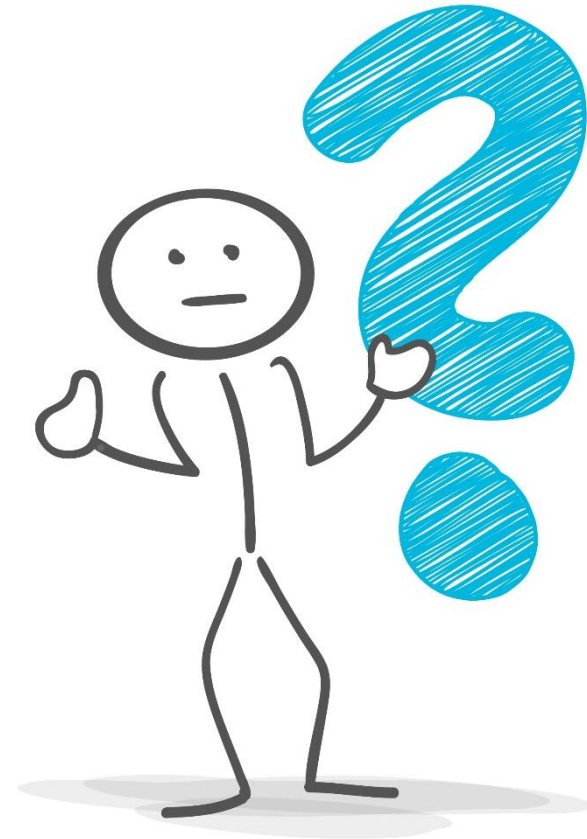
(!) Create an ASTM standard practice

pH testing experience

Water sample preserved at pH=2

- In general: correct reading

- pH 1 and pH 3 can easily be distinguished

  - Reliable results

  - Easy to use

  - …

pH testing experience

Rain water

Type / Brand	Strip read-off
a	5
b	6
c	7

- Different strips give different results

pH testing experience

Desalted water

pH	Read-off A	Read-off B
5	5.5	6.5
5.5	5.5	6.5
6	5.5	6.5
6.5	5.5	6.5
7	5.5	6.5

- pH test strips do not seem to react on changes in pH
- Different strips show different readings

pH testing experience

Urine

pH	Read-off A	Read-off B
5.5	5.5	5.5
6.0	5.0	5.0
6.5	6.5	6.5
7.0	7.0	7.0
7.5	7.5	7.5

• All pH test strips show correct readings

pH testing experience

Summary

pH	Test strip A	Test strip B
pH 2 preserved sample	good	good
Rainwater	Not good	Not good
Desalted water	Not good	Not good
Urine	good	good

pH – uncertainty

pH uncertainty

Typical calibration

"signal"

Linear calibration

Conc. PFAS
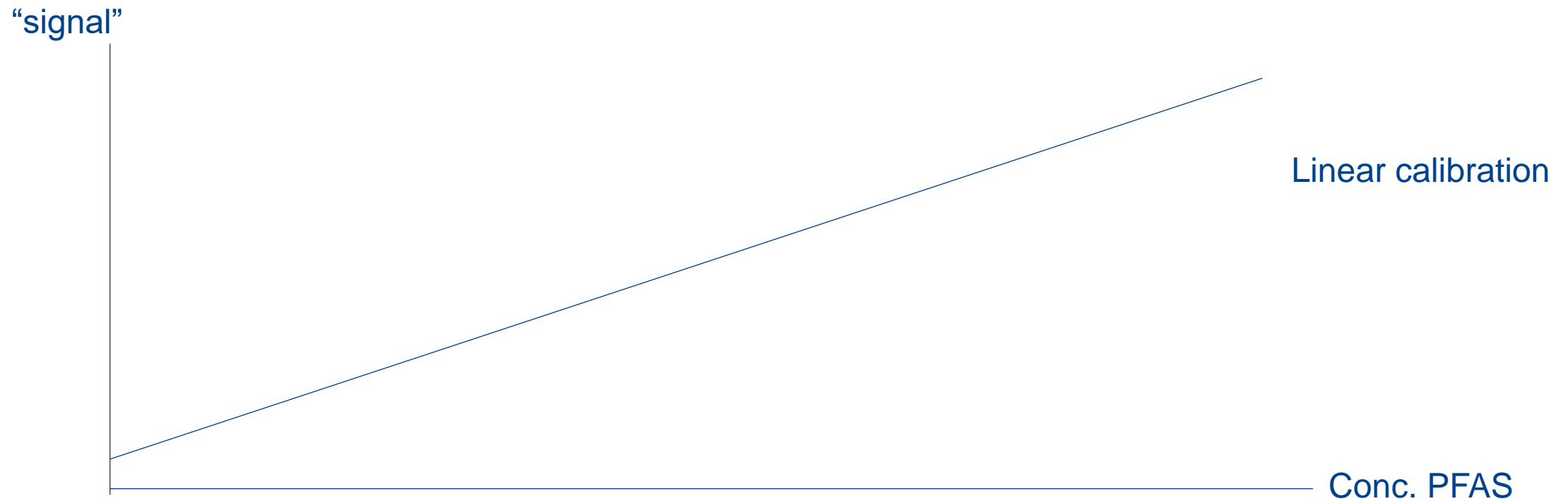
! **Uncertainty lowest in the middle of the range**

pH uncertainty

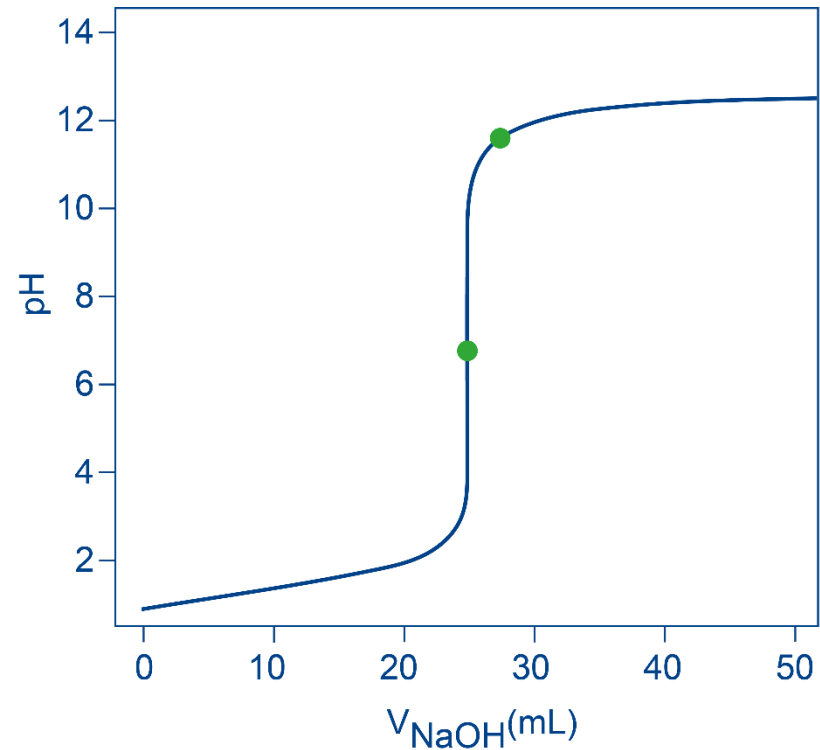**pH – intuitive expectation**

"pH"

Conc. NaOH
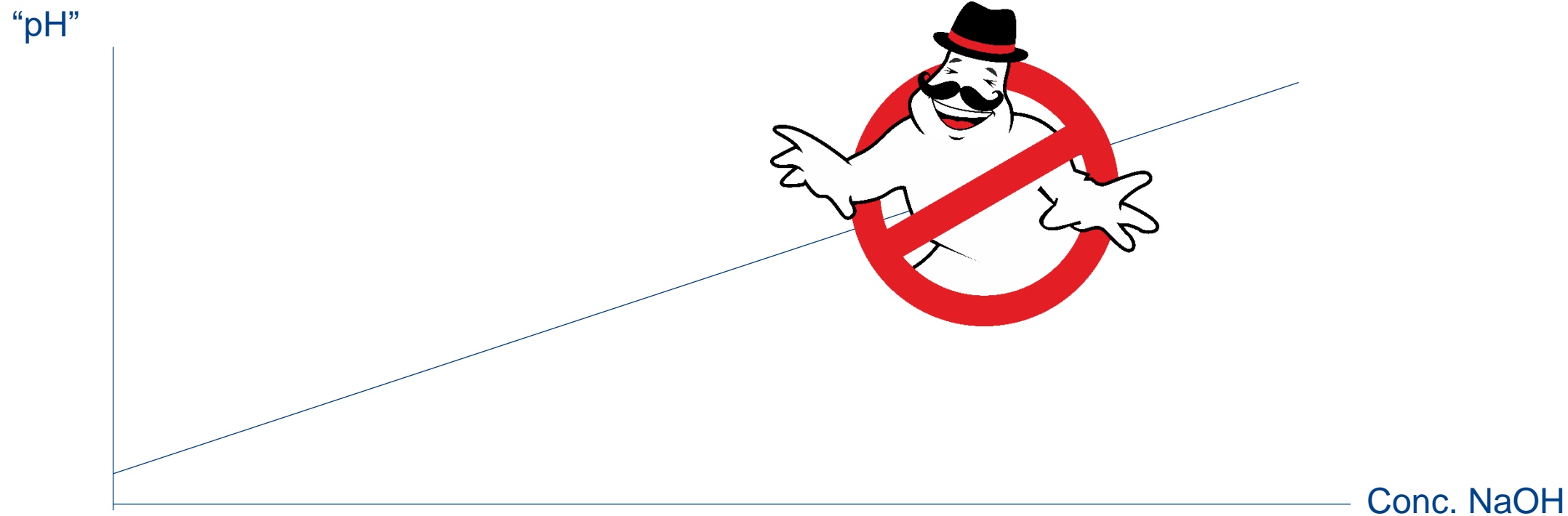
! **pH different from most other analytes**

pH uncertainty

Titration curve

Uncertainty highest in the middle of the range (pH = 7)

pH uncertainty

pH understanding

- Basic definition

  - $pH = -\log_{10}([H_3O^+])\ldots$

  - $[H3O+]*[OH-]=10^{-14}$

- Logarithmic relationship

  - Like exponential relationships very difficult to "feel"

- "Concentration" lowest in the middle of range…

pH uncertainty

Concentration of analyte

- "Analyte" concentration in this case:
  - [H3O+] + [OH-]

pH	$[H_3O^+]$	$[OH^-]$	$[H_3O^+] + [OH^-]$
1	10^{-1}	10^{-13}	10^{-1}
2	10^{-2}	10^{-12}	10^{-2}
7	$\mathbf{10^{-7}}$	$\mathbf{10^{-7}}$	$\mathbf{2*10^{-7}}$
13	10^{-13}	10^{-1}	10^{-1}

← Concentration lowest in the middle of the range

pH uncertainty

Capability of test strips

- Example, Nitrate

  - Detection limit: 10 mg/L

  - Molar weight: 62 g/mol

  - => $1{,}6 * 10^{-3}$ mol/L

- Rule of thumb for test strip detection limits:

  - Regular = about 10^{-3} mol/L

  - High performance = about 10^{-4} mol/L

- Exceptions apply

pH uncertainty

What does it mean for pH-strips?

- Similar limits apply

- In pure (!) water

  - pH test papers should NOT be used in the range pH 4-9

  - Between pH = 4 and pH = 9 papers show a value that is a property of the strip rather than a property of the sample

pH	$[H_3O^+]$	$[OH^-]$	$[H_3O^+] + [OH^-]$
1	10^{-1}	10^{-13}	10^{-1}
3	10^{-3}	10^{-11}	10^{-3}
5	10^{-5}	10^{-9}	10^{-5}
7	10^{-7}	10^{-7}	$2*10^{-7}$
9	10^{-9}	10^{-5}	10^{-5}
11	10^{-11}	10^{-3}	10^{-3}
13	10^{-13}	10^{-1}	10^{-1}

pH uncertainty

What we saw before…

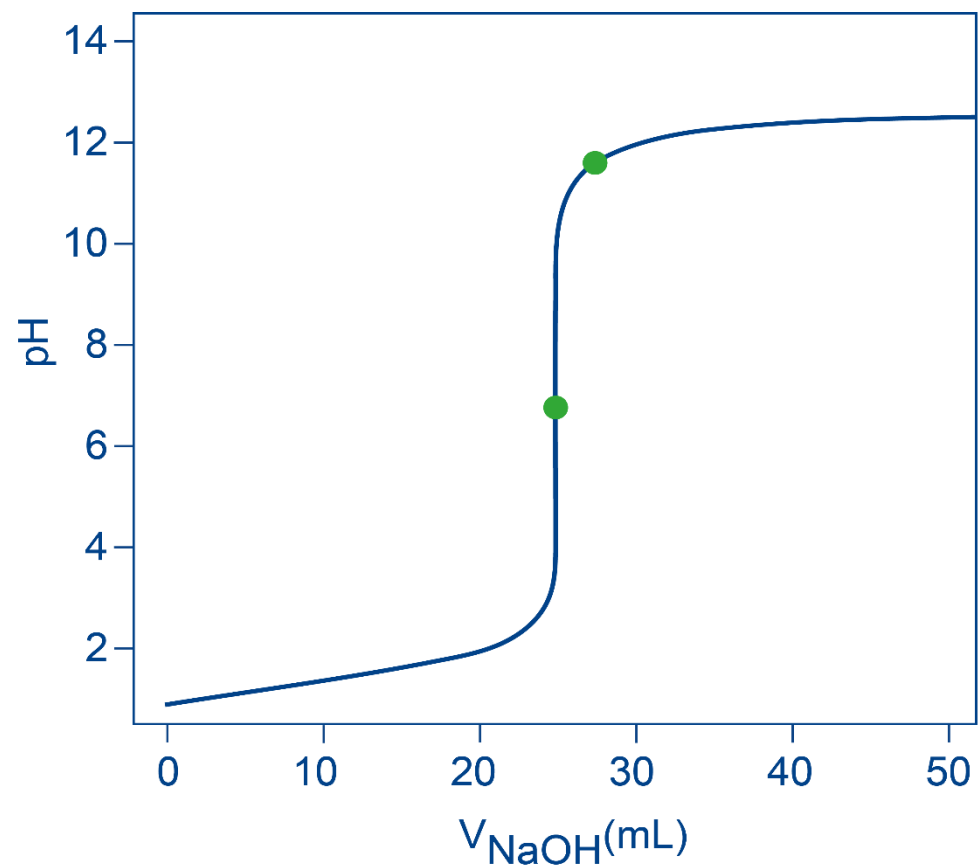| pH	Brand A	Brand B		
pH 2 preserved sample	good	good	←	Understood
Rainwater	Not good	Not good	←	**Understood** (pH between 4 and 9)
Desalted water	Not good	Not good	←	**Understood** (pH between 4 and 9)
Urine	good	good	←	**Why does this work?**

pH buffering

pH buffering

If we only had this…

pH buffering

…nature would be different

- Most processes in nature require a pH of 4-8

- pH 4-8 very difficult to maintain only with strong acids and bases

- Nature provides weak acids and buffer substances

  - Acetic acid / acetate (pH 4.7)

  - Hydrogenphoshate /Dihydrogenphosphate (pH 7.2)

  - Citric acid / citrate (pH 4.2)

  - …

pH buffering

What we saw before…

pH	Brand A	Brand B		
pH 2 preserved sample	good	good	←	Understood
Rainwater	Not good	Not good	←	Understood (pH between 4 and 9)
Desalted water	Not good	Not good	←	Understood (pH between 4 and 9)
Urine	good	good	←	**Understood** (buffering)

What does the Standard Practice say?

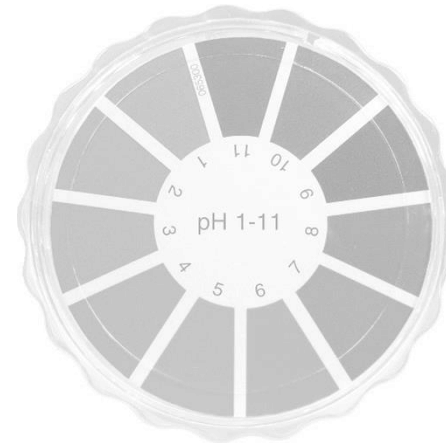# Standard Practice recommendations

- Well buffered solutions

  - pH <3 or pH >10 or Active buffer > 10^{-4} mol/L

- Use of pH test

  - Apply drop to paper

  - Dip into sample

- Typical samples

  - Most body fluids

  - Most surface waters

  - Most solutions in chemical processing

  - Acid stabilized samples

Standard Practice recommendations

- Weakly buffered solutions

  - pH 3-4 or pH 9-10 or Active buffer 10^{-3} - 10^{-4} mol/L

- Use of pH test

  - ~~Apply drop to paper~~

  - Dip into sample

- Typical samples

  - Soft river / lake water

Standard Practice recommendations

- Very weakly buffered solutions

  - pH 4-10 AND active buffer $<10^{-4}$ mol/L

- Use of pH test

  - ~~Apply drop to paper~~

  - ~~Dip into sample~~

- Typical samples

  - DI Water

  - HPLC eluents
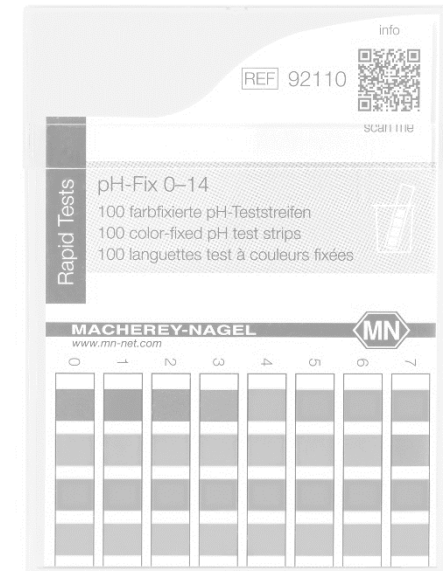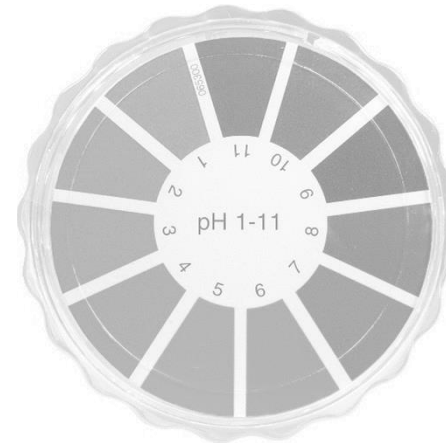
Summary

Summary

ASTM Practice

- Important difference

  - Regularly buffered solutions

  - Weakly buffered solutions

  - Very weakly buffered solutions

- Strip testing is useful for regular and weakly buffered solutions

Thank you for your attention!

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