Application Bulletin 83/5 e

Ω Metrohm

Determination of sodium with the ion-selective electrode

Of interest to:
General analytical laboratories; Water analysis; Pharmaceutical industry; Food analysis
A 1, 2, 4, 7, 12, 16

Summary

The determination of sodium with the sodium ISE represents a selective, rapid, accurate and favorably priced method, which is described in this Bulletin. Examples are used to show how determinations can be carried out with the 692 pH/Ion Meter using either direct measurement or the standard addition technique. The sodium concentration has been determined in standard solutions, water samples (tap water, mineral water, waste water), foodstuffs (spinach, baby food) and urine.

The construction, working principles and areas of application of the two Metrohm ion-selective sodium electrodes – the 6.0501.100 glass membrane ISE and the 6.0508.100 polymer membrane ISE – are explained in detail.

Theory

The activity of ions can be determined by means of ion-selective electrodes. In very dilute solutions the activity corresponds approximately to the concentration of the respective ion.

The fact that in an ideal case ISEs only respond to a particular type of ion means that it is possible to specify the present form of bonding of an ion and to determine it selectively (examples: selective determination of a particular oxidation state of an element; determination of free metal ions in the presence of complexly bound metal ions).

However, ion-selective electrodes that have no cross-sensitivity towards ions that are chemically similar do not exist. ISEs can therefore not be said to be specific.

The use of the two ion-selective sodium electrodes

The measuring range of the glass membrane ISE lies between 1×10^{-5} and 1 mol/L Na^+ (corresponds to 0.23 mg/L ... 22.99 g/L Na^+). Even lower Na^+ concentrations can be determined with the polymer membrane ISE: down to 5×10^{-6} mol/L (0.11 mg/L).

The 6.0501.100 glass membrane ISE is primarily used for samples with a difficult matrix (fruit and vegetable juice; samples containing chlorate, perchlorate and/or chloroacetate ions).

The 6.0508.100 polymer membrane ISE is recommended for the analysis of water samples (ultrapure, rain, ground, surface and drinking water) and for acidic samples containing fluoride, fluoroborate or fluorosilicate ions.

6.0501.100 glass membrane ISE

Construction of the electrode

The electrode shaft and membrane are made of glass. The selectivity for Na^+ ions is determined by the composition of the glass membrane.

Composition and conditioning of the membrane

The glass membrane (composition: Li_2O-Al_2O_3-SiO_2) is immersed in water before use; this generates a gel-like hydrated silicic acid layer.

Working principle

In aqueous solution, cations are removed from the outer hydrated layer and replaced by Na^+ ions from the sample. This creates a potential at the boundary layer between the sample solution and the membrane that depends on the activity of sodium.

ISA solutions

ISA is the abbreviation for **I**onic **S**trength **A**djustor. This is a solution with a high ionic strength that is used to dilute the sample solutions while simultaneously «fixing» their ionic strength. As a result of the almost constant ionic strength, the activity coefficient $\gamma_{\text{meas. ion}}$ remains virtually unchanged, even when measurements are made in very different sample solutions.

Apart from fixing the ionic strength, ISA solutions can also adjust the pH value at the same time. Such solutions are known as **TISAB**: **T**otal **I**onic **S**trength **A**djustment **B**uffer.

In order to remove interfering ions, these sample-conditioning solutions can additionally contain complexing agents. It is thus possible to carry out highly selective measurements even with an electrode that has a relatively low selectivity.

The choice of one of these solutions depends on the particular application. For sodium determinations with the glass membrane ISE it is necessary to use a TISAB solution that also buffers pH values above 9.

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6.0508.100 polymer membrane ISE

Construction of the electrode

The electrode consists of a plastic shaft (PVC), a polymer membrane and an inner Ag/AgCl system. It is filled with an internal buffer containing NaCl.

Composition and conditioning of the membrane

The membrane is made of PVC, plasticizer and ionophore + additive.

It is not necessary to immerse the PVC membrane in water before use, i.e. the polymer membrane ISE is immediately ready for use.

Working principle

The ionophore within the polymer membrane is responsible for the selectivity, i.e. it is able to take up Na^+ ions selectively.

The molecular structure of the ionophore is adapted to suit the coordination number and size of the sodium ion. During the measurement, Na^+ ions diffuse from the sample solution into the polymer membrane. This results in a concentration gradient and therefore a membrane potential.

The polymer has lipophilic properties, i.e. water or ions with a hydration sphere cannot penetrate into the membrane. In aqueous solution, sodium ions are also surrounded by a hydration sphere. However, as a result of the gain in energy this is removed upon inclusion in the ionophore.

ISA solution

The addition of an ISA solution for «fixing» the ionic strength or adjusting the pH value is not necessary if the polymer membrane ISE is used in a concentration range below 50 ppm Na^+. At higher concentrations it is the sample matrix that determines whether an ISA solution is required. pH adjustment with a TISAB solution is not necessary. However, we recommend that the polymer membrane ISE is chiefly used in a pH range between 3 and 12, as longer periods of use outside this range can shorten the service life of the electrode.

Direct measurement with calibration

The ionic concentration of the sample is interpolated using a calibration curve. This curve is obtained by measuring standard solutions. The expected ionic concentration should be approximately in the middle of the concentration range of the standard solutions.

Standard addition

For the standard addition technique, a known sample volume is spiked with a defined quantity of the ion to be determined (possibly in several steps). The ionic concentration of the sample is then calculated automatically from the resulting potential differences between the sample solution alone and the spiked solutions.

The volume of the added standard solution should not exceed 25% of the sample volume. The concentration of the standard solution should be as high as possible (so that dilution effects can be neglected).

There are three types of standard addition: *manual*, *auto dos* and *auto.* The quickest method is the automatic standard addition *auto*. However, please note that in order to obtain accurate results, the chosen potential difference ΔU must be at least 12 mV per addition and that at least three standard additions must be performed (ΔU_{total} at least 30 mV). If exactly defined volumes of the standard additions are required but maximum ease of operation is also desirable, choose *auto dos* and enter the individual volumes (see Instructions for use).

Instruments and accessories

2.692.0010	pH/Ion Meter
2.765.0030	Dosimat Titration Stand
6.3014.213	10 mL Exchange Unit
6.2138.010	Connection cable 692–765
6.0501.100	Sodium-selective glass membrane electrode
6.0508.100	Sodium-selective polymer membrane electrode
6.2104.020	Cable for Na ISE
6.0726.100	Double-junction Ag/AgCl reference electrode (for measurements with the glass membrane ISE)
	Inner electrolyte: c(KCl) = 3 mol/L
	Bridge electrolyte: TISAB solution (see reagents)
6.0733.100	LL Ag/AgCl reference electrode (for measurements with the polymer membrane ISE)
	Reference electrolyte: c(KCl) = 3 mol/L
6.2106.020	Cable for reference electrode
6.1110.100	Pt 1000 temperature sensor
6.2104.080	Cable for temperature sensor
6.1415.220	Titration vessel
6.1414.010	Titration vessel lid
6.2125.060	Connection cable 692–PC
6.2125.010	Adapter cable
6.6008.500	VESUV 3.0 Metrodata software

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Reagents

a) Measurements with the glass membrane ISE

Standard solution	$\beta(Na^+)$ = 2000 mg/L
TISAB solution	c(tris(hydroxymethyl)-aminomethane) = 1 mol/L; pH value adjusted to 8 ... 10 with $c(HNO_3)$ = 2 mol/L.
Conditioning solution	c(NaCl) = 1 mol/L

b) Measurements with the polymer membrane ISE

Standard solution 1	$\beta(Na^+)$ = 2106.9 mg/L
Standard solution 2	$\beta(Na^+)$ = 207.42 mg/L
ISA solution (depending on application)	$c(CaCl_2)$ = 1 mol/L

Electrode handling

The following points must be observed in order to achieve optimal results.

a) Glass membrane ISE

- We recommend that the electrode is shaken like a clinical thermometer prior to the first measurement.
- The glass membrane ISE should be stored dry if it is out of use for longer periods of time. For short-term storage c(NaCl) = 0.1 mol/L is suitable.
- Before being used for the first time, and after longer periods out of use, the glass membrane must be activated/conditioned by overnight immersion in c(NaCl) = 1 mol/L.
- With the reference electrode care should be taken that the internal parts are well wetted. Any air bubbles formed when the electrolyte is filled in must be removed.
- After each measurement the electrode must be thoroughly rinsed with dist. water and wiped off with a slightly moist tissue.
- Potassium interferes if present in 500-fold excess compared to sodium.
- As under acidic conditions this Na ISE responds to H_3O^+ ions like a pH glass electrode, measurements must be carried out under alkaline conditions (pH = 8 ... 10).
- Other ions that interfere are listed in the Instructions for use of the electrode.

b) Polymer membrane ISE

- It is not necessary to shake the polymer membrane ISE before it is used for the first time; the electrode can be used immediately.
- If the electrode is not to be used for some time it should be stored dry.
- A long conditioning period for the membrane before use is not necessary with this Na ISE. Briefly rinsing the electrode with dist. water and drying it with a soft paper tissue prior to the measurement is completely adequate.
- Avoid touching the polymer membrane with your fingers.
- In contrast to the glass membrane ISE it is not necessary to work with a double-junction reference electrode. A bridge electrolyte (TISAB solution for the glass membrane ISE) is not required. c(KCl) = 3 mol/L as reference electrolyte yields excellent results as regards accuracy and precision.
- There must be no air bubbles on the membrane surface before and during the measurements.
- The polymer membrane ISE should neither be cleaned with nor stored in organic solvents (acetone, ethanol).
- Use at increased temperatures (>30 °C) should be avoided if possible.
- The electrode should not be used for longer periods of time at extreme pH values, as solutions whose pH value is not between 3 and 12 shorten the service life of the polymer membrane ISE.
- If a series of determinations is to be carried out then the electrode should be stored in dist. water between the measurements instead of just rinsing and drying it. In this way any Na^+ ions that may have diffused into the membrane during the previous determination can be rinsed out of it again. The working procedure described yields better results with regard to accuracy and precision.

General information

- All solutions must be stored in plastic vessels.
- All standard additions must be performed with stirring (stirrer parameter 692: *ON* or *control.*). Take care that the stirrer is switched on and that there is a stirrer bar in the titration vessel. Additions without stirring result in incorrect measurements!
- Method selection:

  Standard addition is a rapid and reliable method, particularly for an undefined sample matrix. A direct measurement is advisable whenever many determinations have to be carried out one after another in similar solutions with a defined and unproblematic sample matrix.
- The addition of TISAB solution before measurements with the glass membrane ISE has the effect that the ionic strength and the pH value of the sample solutions remain constant.
- If the automatic standard addition *auto* is used for solutions with low ionic strength, the obtained potential steps can slightly differ from the defined parameter *delta U*. However, this does not affect the accuracy of the analytical results.
- Choice of the standard concentration:

  In order to ensure a correct evaluation of the standard addition by the 692 pH/Ion Meter, the standard concentrations c_{std} for the different buret volumes V_{buret} must be chosen as a function of the

sample concentration c_{smpl} according to the following table:

V_{buret}/mL	$C_{std} : c_{smpl}$
5	40 : 1
10	20 : 1
20	10 : 1
50	5 : 1

If the sample has been greatly diluted with ISA or TISAB solution this ratio must be taken into account.

Example:

Sample concentration c_{smpl}	5 mg/L
Buret volume V_{buret}	10 mL
Sample volume	10 mL
Volume ISA/TISAB	10 mL
Total volume V_{total}	20 mL
Factor $c_{std} : c_{smpl}$ from the table	20

This yields a sample concentration of 2.5 mg/L in the titration vessel. The optimal concentration of the standard is therefore 2.5 mg/L x 20 = 50 mg/L.

Please note that this only provides a rough guideline for the standard concentration. Accurate measurements are also possible if the above recommendations are not strictly adhered to.

- The equations for calculating the results are explained in the Instructions for use of the 692 pH/Ion Meter in paragraphs 3.1 and 3.2.

- Low sodium concentrations:

  In this case the response time is distinctly longer. The blank values of the reagents used must be taken into account.

a) Measurements with the glass membrane ISE

Direct measurement

Please observe the information given in the Instructions for use of the 692 pH/Ion Meter.

The following calibration is an example of a sample with an unproblematic matrix.

Sample:	NaCl solution with 230 mg/L Na^+
Sample volume:	20 mL
Volume of TISAB:	20 mL
Standard:	2000 mg/L Na^+ in 10 mL Exchange Unit
Concentration range:	50 ... 300 mg/L Na^+
No. of calibration points:	6

Parameters

```
692 pH/Ion Meter      ON1/109  692.0020
date   96-03-13   time  08:52:54
parameter
  meas.type:          direct
>measuring parameters
  ion type:           Na(+1)
  conc.unit:          mg/l
  meas.input:         1
  electr.id:          0501.100
  drift               0.5 mV/min
  temperature         25.0  C
  method id           NA
  delta measurement:  OFF
  stirrer:            control
  prestir pause       10  s
  stir time           90  s
  poststir pause      20  s
>calculation parameters
  smpl size           20.0 ml
  V total             40.0 ml
  factor              1.0
  smpl size unit:     ml
>calibration parameters
  temperature         25.0  C
  drift               0.5 mV/min
  report:             full
  no.of standards     6
  addition:           auto
  min.conc.           50.0 mg/l
  max.conc.           300.0 mg/l
  V init              40.0 ml
  no.of Exchange Units 1
  conc.1              2000.0 mg/l
  V Exchange Unit 1:  10 ml
>analog output
  select:             Conc
  state:              OFF
>limits Conc
  state:              OFF
>limits T
  state:              OFF
>plot parameters
  left mar.           0.0E+00 mg/l
  right mar.          1.0E+30 mg/l
  left marg.T         20  C
  right marg.T        30  C
>preselections
  req.ident:          OFF
  req.smpl size:      value
      --------------
```

Configuration

```
692 pH/Ion Meter      ON1/109  692.0020
date   96-03-13   time  08:52:24
config
>printer
  id1                 ISE Na
  id2                 AB Nr. 83/4
  print header:       always
  character set:      Epson
>print meas.value
  print crit:         drift
  date&time:          ON
>auxiliaries
  last digit:         ON
  dialog:             english
  date                96-03-13
  time                08:52:25
  temp.unit:          C
  run number          0
  Dosimat:            665
  device label
  program             692.0020
>RS232 settings
  baud rate:          9600
  data bit:           8
  stop bit:           1
  parity:             none
  handshake:          HWs
  RS control:         ON
      --------------
```

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Calibration

```
692 pH/Ion Meter         ON1/109  692.0020
date   96-03-12   time  16:37:52      31
Conc          NA    electr.id       0501.100
conc.calibration
   meas.input:                  1
   ion type               Na(+1)
   temperature man.         25.0  C
   cal.date     96-03-12  16:37

              conc/mg/l      U/mV     dconc/%
   std. 1     5.00E+01      109.5       0.0
   std. 2     7.15E+01      118.7      -0.1
   std. 3     1.02E+02      127.8       0.0
   std. 4     1.47E+02      137.1       0.0
   std. 5     2.10E+02      146.2       0.1
   std. 6     3.00E+02      155.5      -0.1
```
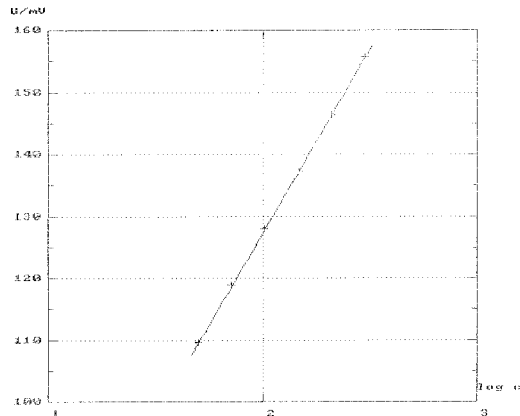


```
variance             0.001
slope               59.1 mV
E(0)                 9.0 mV
===============
```

Results

```
692 pH/Ion Meter         ON1/109  692.0020
date   96-03-12   time  16:50:36
Conc          NA    electr.id       0501.100
id1              ISE Na
id2              AB Nr. 83/4
smpl size            5.0 ml
#35      231 mg/l                   Na(+1)
    96-03-12  16:50:36
          ===============
```

```
692 pH/Ion Meter         ON1/109  692.0020
date   96-03-12   time  16:50:50
Conc          NA    electr.id       0501.100
id1              ISE Na
id2              AB Nr. 83/4
smpl size            5.0 ml
#36      231 mg/l                   Na(+1)
    96-03-12  16:50:50
          ===============
```

```
692 pH/Ion Meter         ON1/109  692.0020
date   96-03-12   time  16:51:06
Conc          NA    electr.id       0501.100
id1              ISE Na
id2              AB Nr. 83/4
smpl size            5.0 ml
#37      231 mg/l                   Na(+1)
    96-03-12  16:51:06
          ===============
```

Result of a threefold determination:

Mean value: 231 mg/L Na$^+$

s_{abs}:   1 mg/L Na$^+$

s_{rel}:   0.4%

Standard addition

Please observe the information given in the Instructions for use of the 692 pH/Ion Meter.

Example of determining the concentration by standard addition:

Sample:	NaCl solution with 57.5 mg/L Na$^+$
Sample volume:	20 mL
Volume of TISAB:	20 mL
Standard:	2000 mg/L Na$^+$ in 10 mL Exchange Unit
No. of additions:	5

Parameters

```
692 pH/Ion Meter         ON1/109  692.0020
date   96-03-11   time  15:18:24
parameter
   meas.type:           std.add
>measuring parameters
   ion type:            Na(+1)
   conc.unit:             mg/l
   meas.input:              1
   electr.id:           0501.100
   drift               0.5 mV/min
   temperature         25.0  C
   method id             NA
   stirrer:            control
   prestir pause        10 s
   stir time            90 s
   poststir pause       20 s
>calculation parameters
   smpl size          20.0 ml
   V total            40.0 ml
   factor              1.0
   smpl size unit:      ml
>standard addition
   type:                add
   conc.std.         2000.0 mg/l
   report:             full
   addition:           auto
   delta U              12 mV
   dos.rate:           medium
   no.of additions       5
   V Exchange Unit:     10
   activate pulse:      OFF
   stop V             10.0 ml
>preselections
   req.ident:           OFF
   req.smpl size:      value
   --------------
```

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Result

```
692 pH/Ion Meter         ON1/109  692.0020
date   96-03-11   time  14:17:56      27
Conc      NA     electr.id       0501.100
id1           ISE Na
id2           AB Nr. 83/4
addition/subtraction method
  meas.type:           std.add
  meas.input:              1
  temperature man.       25.0  C
  conc.std             2000.0  mg/l
  V total                40.0  ml
  initial voltage        93.5  mV
  smpl size              20.0  ml

                dV/ml     U/mV    dU/mV
  std.incr. 1   0.349    105.4    11.9
  std.incr. 2   0.569    117.3    11.9
  std.incr. 3   0.935    129.2    11.9
  std.incr. 4   1.463    140.5    11.3
  std.incr. 5   2.552    152.2    11.7
```
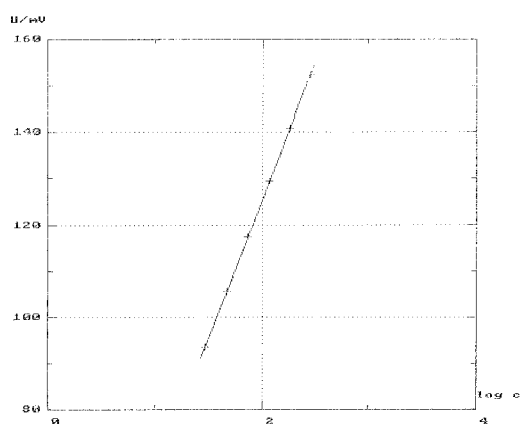


```
variance              0.001
slope                60.0  mV
E(0)                  5.1  mV
Na(+1)               59.4  mg/l
```

Result:

Measured value:	59.4 mg/L Na$^+$
Theoretical value:	57.5 mg/L Na$^+$
Absolute deviation:	1.9 mg/L Na$^+$
Relative deviation:	3.3%

b) Measurements with the polymer membrane ISE

Direct measurement

The following calibration is an example of a sample with an unproblematic matrix.

Sample:	solution with 207.42 mg/L Na$^+$
Sample volume:	40 mL
Standard:	2106.9 mg/L Na$^+$ in 10 mL Exchange Unit
Concentration range:	50 ... 300 mg/L Na$^+$
No. of calibration points:	6

Parameters

```
692 pH/Ion Meter                    692.0021
date  2001-05-22   time  08:58:12
parameter
  meas.type:             direct
>measuring parameters
  ion type:              Na(+1)
  conc.unit:             ppm
  meas.input:            1
  electr.id:             0508.100
  drift                  0.1  mV/min
  method id              ********
  delta measurement:     OFF
  stirrer:               control
  prestir pause          10  s
  stir time              90  s
  poststir pause         20  s
>calculation parameters
  smpl size              40.0  ml
  V total                40.0  ml
  factor                 1.0
  smpl size unit:        ml
>calibration parameters
  drift                  0.5  mV/min
  report:                full
  cal.interval           OFF  h
  no.of standards        6
  addition:              auto
  min.conc.              50.0  ppm
  max.conc.              300.0  ppm
  V init                 40.0  ml
  no.of Exchange Units   1
  conc.1                 2106.9  ppm
  V Exchange Unit 1:     10  ml
>analog output
  select:                Conc
  state:                 ON
  0 mV at                1.00E-03  ppm
  1 V range              100.00  ppm
>limits Conc
  state:                 OFF
>limits T
  state:                 OFF
>plot parameters
  left mar.              0.0E+00  ppm
  right mar.             1.0E+30  ppm
  left marg.T            20  °C
  right marg.T           30  °C
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
```

Configuration

```
692 pH/Ion Meter          692.0021
date  2001-05-11  time  14:47:09
config
>printer
   id1        Na ISE/ Polymer
   id2        AB Nr. 83/5
   print header:       always
   calibration report:     ON
   character set:      Seiko
>print meas.value
   print crit:         drift
   date&time:          ON
>auxiliaries
   last digit:         ON
   dialog:             english
   date             2001-05-11
   time             14:47:10
   temp.unit:          C
   run number          9
   Dosimat:            665
   device label    692-1
   program          692.0021
>RS232 settings
   baud rate:          9600
   data bit:           7
   stop bit:           1
   parity:             even
   handshake:          HWs
   RS control:         ON
   ---------------
```
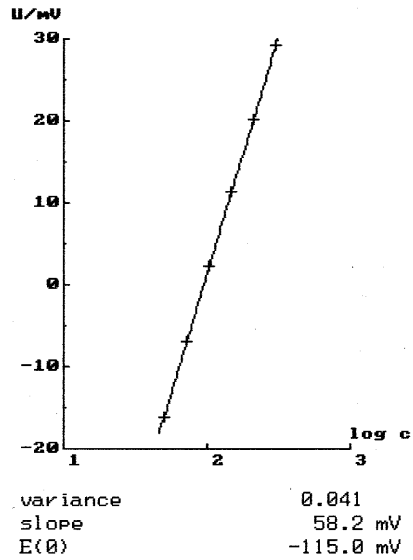
Calibration

```
692 pH/Ion Meter          692.0021
date  2001-05-22  time  08:59:17      1
Conc  *******   electr.id   0508.100
conc.calibration
   meas.input:              1
   ion type            Na(+1)
   temperature          23.6 °C
   c.dat.   2001-05-22  08:35
```

	conc/ppm	U/mV	dconc/%
std. 1	5.00E+01	-16.4	0.8
std. 2	7.15E+01	-7.1	0.0
std. 3	1.02E+02	2.2	-1.0
std. 4	1.46E+02	11.2	-0.6
std. 5	2.10E+02	20.0	0.1
std. 6	3.00E+02	29.0	0.7


```
variance        0.041
slope           58.2 mV
E(0)           -115.0 mV
-----------------
```

Results

```
692 pH/Ion Meter          692.0021
date  2001-05-22  time  09:06:56
Conc  *******   electr.id   0508.100
id1        Na ISE/ Polymer
id2        AB Nr. 83/5
smpl size          40.0 ml
#2      206 ppm      23.5 °C     Na(+1)


692 pH/Ion Meter          692.0021
date  2001-05-22  time  09:10:50
Conc  *******   electr.id   0508.100
id1        Na ISE/ Polymer
id2        AB Nr. 83/5
smpl size          40.0 ml
#3      209 ppm      23.3 °C     Na(+1)
   2001-05-22  09:10:50
        ==============


692 pH/Ion Meter          692.0021
date  2001-05-22  time  09:15:45
Conc  *******   electr.id   0508.100
id1        Na ISE/ Polymer
id2        AB Nr. 83/5
smpl size          40.0 ml
#4      210 ppm      23.0 °C     Na(+1)
   2001-05-22  09:15:45
        ==============
```

Result of a sevenfold determination:

Mean value: 210.43 mg/L Na^{+}

s_{abs}:   2.37 mg/L Na^{+}

s_{rel}:   1.13%

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Standard addition

Example of determining the concentration by standard addition:

Sample:	solution with 46 mg/L Na^+
Sample volume:	40 mL
Standard:	2106.9 mg/L Na^+ in 10 mL Exchange Unit
No. of additions:	5

Parameters

```
692 pH/Ion Meter            692.0021
date 2001-05-11  time  11:57:26
parameter
  meas.type:       std.add
>measuring parameters
  ion type:        Na(+1)
  conc.unit:       ppm
  meas.input:      1
  electr.id:       0508.100
  drift            0.1 mV/min
  method id        Na3
  stirrer:         control
  prestir pause    10 s
  stir time        90 s
  poststir pause   20 s
>calculation parameters
  smpl size        40.0 ml
  V total          40.0 ml
  factor           1.0
  smpl size unit:  ml
>standard addition
  type:            add
  conc.std.        2106.9 ppm
  report:          full
  addition:        auto
  delta U          12 mV
  dos.rate:        medium
  no.of additions  5
  V Exchange Unit: 10
  activate pulse:  OFF
  stop V           10.0 ml
>preselections
  req.ident:       OFF
  req.smpl size:   value
  -------------
```

Configuration

```
692 pH/Ion Meter            692.0021
date 2001-05-11  time  11:57:24
config
>printer
  id1       Na ISE/ Polymer
  id2          AB Nr. 83/5
  print header:      always
  calibration report:    OFF
  character set:        Seiko
>print meas.value
  print crit:       immediate
  date&time:            ON
>auxiliaries
  last digit:           ON
  dialog:          english
  date             2001-05-11
  time              11:57:24
  temp.unit:            C
  run number            6
  Dosimat:            665
  device label     692-1
  program          692.0021
>RS232 settings
  baud rate:         9600
  data bit:          7
  stop bit:          1
  parity:          even
  handshake:        HWs
  RS control:         ON
  -------------
```

Result

```
692 pH/Ion Meter            692.0021
date 2001-05-11  time  09:03:29     2
Conc      Na3   electr.id    0508.100
id1    Na ISE/ Polymer
id2       AB Nr. 83/5
addition/subtraction method
  meas.type:       std.add
  meas.input:          1
  temperature        24.0 C
  conc.std         2106.9 ppm
  V total           40.0 ml
  initial voltage   -33.0 mV
  smpl size         40.0 ml
```

	dV/ml	U/mV	dU/mV
std.incr. 1	0.400	-23.9	9.1
std.incr. 2	0.582	-14.8	9.1
std.incr. 3	0.915	-5.3	9.5
std.incr. 4	1.472	4.4	9.7
std.incr. 5	2.393	14.2	9.8

Metrohm
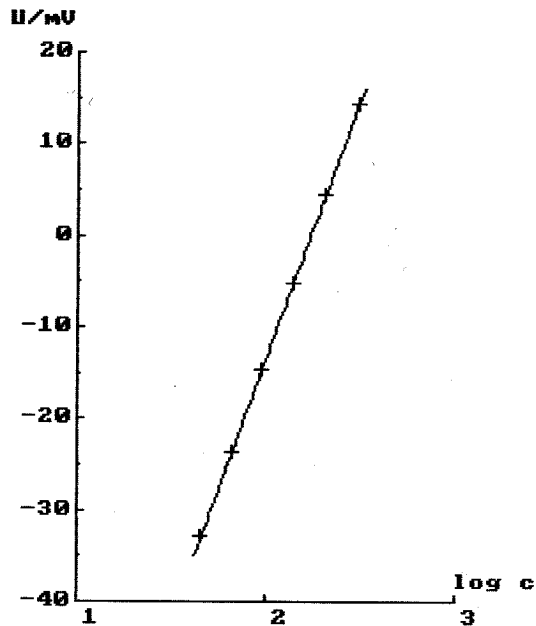
variance	0.002
slope	57.3 mV
E(0)	-128.1 mV
Na(+1)	45.7 ppm

===============

Result of a tenfold determination:

Mean value: 45.66 mg/L Na$^+$

s_{abs}: 0.66 mg/L Na$^+$

s_{rel}: 1.45%

Practical examples

1. Sodium in the inlet of a waste water treatment plant using automatic standard addition

|	
Electrode:	glass membrane ISE
Sample preparation:	Sample is diluted 1 : 4 with dist. water ($\rightarrow$ factor = 4).
Analysis:	20 mL sample solution and 20 mL TISAB solution are pipetted into the titration vessel.
Standard:	$\beta(Na^+)$ = 2000 mg/L
No. of additions:	5

Parameters

```
692 pH/Ion Meter       ON1/109  692.0020
date   96-03-13   time   08:19:20
parameter
  meas.type:            std.add
>measuring parameters
  ion type:             Na(+1)
  conc.unit:            mg/l
  meas.input:           1
  electr.id:            0501.100
  drift                 0.5 mV/min
  temperature           25.0  C
  method id             NA
  stirrer:              control
  prestir pause         10 s
  stir time             90 s
  poststir pause        20 s
>calculation parameters
  smpl size             20.0 ml
  V total               40.0 ml
  factor                4.0
  smpl size unit:       ml
>standard addition
  type:                 add
  conc.std.             2000.0 mg/l
  report:               full
  addition:             auto
  delta U               12 mV
  dos.rate:             medium
  no.of additions       5
  V Exchange Unit:      10
  activate pulse:       OFF
  stop V                10.0 ml
>preselections
  req.ident:            OFF
  req.smpl size:        value
        -----------------
```

Result

```
692 pH/Ion Meter       ON1/109  692.0020
date   96-03-11   time   17:08:31      34
Conc          NA   electr.id     0501.100
id1           ISE Na
id2           ARA in
addition/subtraction method
  meas.type:            std.add
  meas.input:           1
  temperature man.      25.0  C
  conc.std              2000.0 mg/l
  V total               40.0 ml
  initial voltage       96.8 mV
  smpl size             5.0 ml
```

	dV/ml	U/mV	dU/mV
std.incr. 1	0.415	108.8	12.0
std.incr. 2	0.675	120.8	12.0
std.incr. 3	1.035	132.2	11.4
std.incr. 4	1.750	143.7	11.5
std.incr. 5	2.957	155.1	11.4
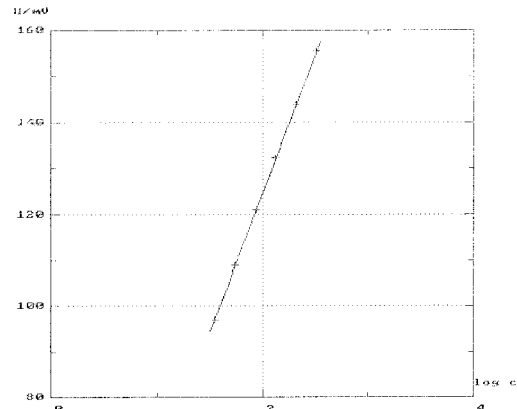
variance	0.001
slope	60.5 mV
E(0)	3.4 mV
Na(+1)	280 mg/l

Ω Metrohm

Result of a fourfold determination:

Mean value: 285 mg/L Na$^+$

S_{abs}: 5 mg/L Na$^+$

S_{rel}: 1.7%

2. Sodium in the outlet of a waste water treatment plant using automatic standard addition

Electrode: glass membrane ISE

Sample preparation: not required

Analysis: 15 mL sample and 25 mL TISAB solution are pipetted into the titration vessel.

Standard: $\beta(Na^+)$ = 2000 mg/L

No. of additions: 5

Parameters

```
692 pH/Ion Meter      ON1/109  692.0020
date   96-03-12   time  13:16:22
parameter
  meas.type:            std.add
>measuring parameters
  ion type:             Na(+1)
  conc.unit:            mg/l
  meas.input:           1
  electr.id:            0501.100
  drift                 0.5 mV/min
  temperature           25.0  C
  method id             NA
  stirrer:              control
  prestir pause         10 s
  stir time             90 s
  poststir pause        20 s
>calculation parameters
  smpl size             15.0 ml
  V total               40.0 ml
  factor                1.0
  smpl size unit:       ml
>standard addition
  type:                 add
  conc.std.             2000.0 mg/l
  report:               full
  addition:             auto
  delta U               12 mV
  dos.rate:             medium
  no.of additions       5
  V Exchange Unit:      10
  activate pulse:       OFF
  stop V                10.0 ml
>preselections
  req.ident:            OFF
  req.smpl size:        value
  ---------------
```

Result

```
692 pH/Ion Meter      ON1/109  692.0020
date  96-03-12   time  10:50:50       8
Conc        NA    electr.id      0501.100
id1            ISE Na
id2            ARA out
addition/subtraction method
  meas.type:         std.add
  meas.input:        1
  temperature man.   25.0   C
  conc.std           2000.0 mg/l
  V total            40.0 ml
  initial voltage    98.6 mV
  smpl size          15.0 ml

               dV/ml    U/mV    dU/mV
  std.incr. 1  0.406   110.5    11.9
  std.incr. 2  0.660   122.4    11.9
  std.incr. 3  1.092   134.1    11.7
  std.incr. 4  1.855   145.8    11.7
  std.incr. 5  3.298   157.4    11.6
```
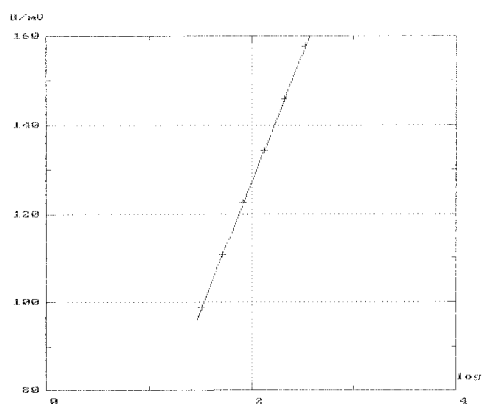


```
variance               0.000
slope                  57.9 mV
E(0)                   11.0 mV
Na(+1)                 86.3 mg/l
            ===============
```

Result of fivefold determination:

Mean value: 87.3 mg/L Na$^+$

S_{abs}: 0.7 mg/L Na$^+$

S_{rel}: 0.8%

3. Sodium in spinach (salted cream spinach) using automatic standard addition

Electrode: glass membrane ISE

Sample preparation: Approx. 10 g sample (package information: 1% NaCl) is stirred for 15 min with 100 mL dist. water. The sample is filtered and the filtrate made up to 200 mL.

Analysis: 10 mL sample solution ($\rightarrow$ factor = 20), 10 mL dist. water and 20 mL TISAB solution are pipetted into the titration vessel.

Standard: $\beta(Na^+)$ = 2000 mg/L; this corresponds to w(NaCl) = 0.508%

No. of additions: 4

Metrohm

Parameters

```
692 pH/Ion Meter       ON1/109  692.0020
date   96-03-13    time  08:34:44
parameter
  meas.type:          std.add
>measuring parameters
  ion type:           Na(+1)
  conc.unit:               %
  meas.input:              1
  electr.id:          0501.100
  drift                  0.5 mV/min
  temperature           25.0  C
  method id              NA
  stirrer:            control
  prestir pause          10 s
  stir time              90 s
  poststir pause         20 s
>calculation parameters
  smpl size            9.35 g
  V total              40.0 ml
  factor               20.0
  smpl size unit:          g
>standard addition
  type:                add
  conc.std.           0.508 %
  report:              full
  addition:            auto
  delta U                12 mV
  dos.rate:           medium
  no.of additions         4
  V Exchange Unit:       10
  activate pulse:      OFF
  stop V               10.0 ml
>preselections
  req.ident:           OFF
  req.smpl size:       value
              ---------------
```
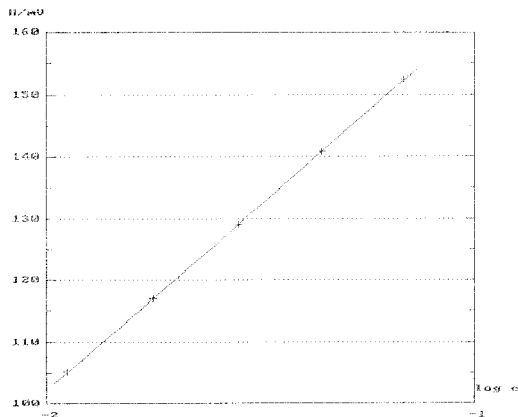
Result

```
692 pH/Ion Meter       ON1/109  692.0020
date   96-03-12    time  18:12:58      44
Conc        NA   electr.id    0501.100
id1       ISE Na
id2       Spinat NaCl
addition/subtraction method
  meas.type:          std.add
  meas.input:              1
  temperature man.     25.0  C
  conc.std            0.508 %
  V total             40.0 ml
  initial voltage    104.9 mV
  factor              20.0
  smpl size            9.35 g
```

	dV/ml	U/mV	dU/mV
std.incr. 1	0.532	116.9	12.0
std.incr. 2	0.868	128.9	12.0
std.incr. 3	1.416	140.6	11.7
std.incr. 4	2.398	152.2	11.6


```
variance            0.001
slope              60.1 mV
E(0)              222.3 mV
Na(+1)             0.958 %
              ---------------
```

Result of a fourfold determination:

Mean value: 0.952% NaCl

S_{abs}:   0.049% NaCl

S_{rel}:   4.9%

4. Sodium in urine using automatic standard addition

Electrode: glass membrane ISE

Sample preparation: Sample is diluted 1 : 40 with dist. water ($\rightarrow$ factor = 40).

Analysis: 20 mL sample solution and 20 mL TISAB solution are pipetted into the titration vessel.

Standard: $\beta(Na^+)$ = 2000 mg/L

No. of additions: 4

Parameters
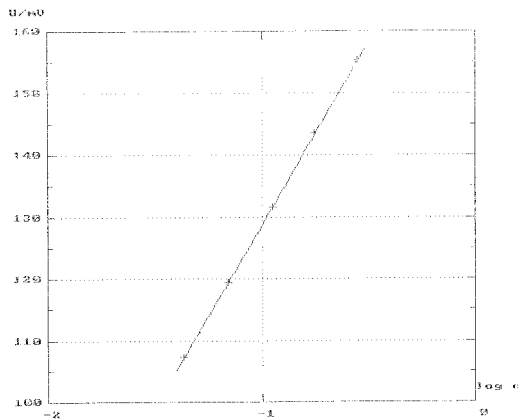
```
692 pH/Ion Meter       ON1/109  692.0020
date   96-03-14    time  13:39:56
parameter
  meas.type:          std.add
>measuring parameters
  ion type:           Na(+1)
  conc.unit:              g/l
  meas.input:              1
  electr.id:          0501.100
  drift                  0.5 mV/min
  temperature           25.0  C
  method id              NA
  stirrer:            control
  prestir pause          10 s
  stir time              90 s
  poststir pause         20 s
>calculation parameters
  smpl size            20.0 ml
  V total              40.0 ml
  factor               40.0
  smpl size unit:          ml
>standard addition
  type:                add
  conc.std.            2.0 g/l
  report:              full
  addition:            auto
  delta U                12 mV
  dos.rate:           medium
  no.of additions         4
  V Exchange Unit:       10
  activate pulse:      OFF
  stop V               10.0 ml
>preselections
  req.ident:           OFF
  req.smpl size:       value
              ---------------
```

Ω **Metrohm**

Result

```
692 pH/Ion Meter        ON1/109   692.0020
date    96-03-14   time  13:05:41         8
Conc        NA     electr.id      0501.100
id1              ISE Na
id2              Urin
addition/subtraction method
   meas.type:            std.add
   meas.input:               1
   temperature man.       25.0   C
   conc.std                2.0 g/l
   V total                40.0 ml
   initial voltage       107.1 mV
   factor                 40.0
   smpl size              20.0 ml

                dV/ml     U/mV    dU/mV
   std.incr. 1  0.545    119.3    12.2
   std.incr. 2  0.910    131.5    12.2
   std.incr. 3  1.507    143.4    11.9
   std.incr. 4  2.602    155.1    11.7
```



```
variance              0.001
slope                58.9 mV
E(0)                187.6 mV
Na(+1)                3.45 g/l
        ---------------
```

Result of a fivefold determination:

Mean value: 3.44 g/L Na$^+$

S_{abs}:   0.03 g/L Na$^+$

S_{rel}:   1.0%

5. Sodium in tap water using automatic standard addition

Electrode:	polymer membrane ISE
Sample preparation:	not required
Analysis:	40 mL tap water (taken at 25 °C after 1 min flow time) is pipetted into the titration vessel.
Standard:	$\beta(Na^+)$ = 207.42 mg/L
No. of additions:	5

Parameters

```
692 pH/Ion Meter                 692.0021
date  2001-05-09  time  15:48:59
parameter
   meas.type:           std.add
>measuring parameters
   ion type:            Na(+1)
   conc.unit:           ppm
   meas.input:          1
   electr.id:           0508.100
   drift                0.1 mV/min
   method id            Natrium
   stirrer:             control
   prestir pause        10 s
   stir time            90 s
   poststir pause       20 s
>calculation parameters
   smpl size            40.0 ml
   V total              40.0 ml
   factor               1.0
   smpl size unit:      ml
>standard addition
   type:                add
   conc.std.            207.42 ppm
   report:              full
   addition:            auto
   delta U              12 mV
   dos.rate:            medium
   no.of additions      5
   V Exchange Unit:     10
   activate pulse:      OFF
   stop V               10.0 ml
>preselections
   req.ident:           OFF
   req.smpl size:       value
```

Ω Metrohm

Configuration

692 pH/Ion Meter   692.0021
date 2001-05-09 time 15:49:50
config
>printer
  id1   Na ISE/ Polymer
  id2   AB Nr. 83/5
  print header: always
  calibration report: OFF
  character set: Seiko
>print meas.value
  print crit: immediate
  date&time: ON
>auxiliaries
  last digit: ON
  dialog: english
  date   2001-05-09
  time   15:49:51
  temp.unit: C
  run number   1
  Dosimat: 665
  device label   692-1
  program   692.0021
>RS232 settings
  baud rate: 9600
  data bit: 7
  stop bit: 1
  parity: even
  handshake: HWs
  RS control: ON
  _____

Result

692 pH/Ion Meter   692.0021
date 2001-05-09 time 14:58:57   4
Conc   Natrium electr.id   0508.100
id1   Na ISE/ Polymer
id2   AB Nr. 83/5
addition/subtraction method
  meas.type: std.add
  meas.input: 1
  temperature   24.8 C
  conc.std   207.42 ppm
  V total   40.0 ml
  initial voltage -107.3 mV
  smpl size   40.0 ml

	dV/ml	U/mV	dU/mV
std.incr. 1	0.415	-97.9	9.4
std.incr. 2	0.640	-88.1	9.8
std.incr. 3	0.934	-78.6	9.5
std.incr. 4	1.378	-69.4	9.2
std.incr. 5	2.116	-60.3	9.1
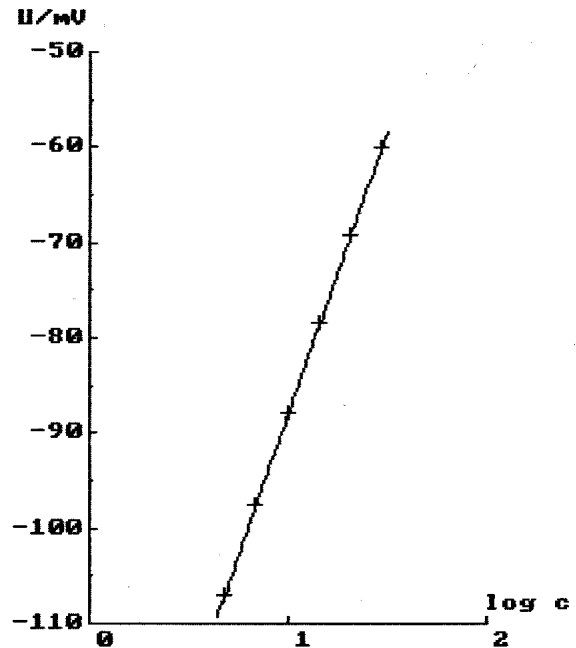
variance	0.000
slope	59.6 mV
E(0)	-147.6 mV
Na(+1)	4.74 ppm

===============

Result of an eightfold determination:

Mean value: 4.74 mg/L Na$^+$

s_{abs}:   0.04 mg/L Na$^+$

s_{rel}:   0.86%

6. Sodium in mineral water using automatic standard addition

Electrode: polymer membrane ISE

Sample preparation: not required

Analysis: 40 mL mineral water (without carbon dioxide) is pipetted into the titration vessel.

Standard: $\beta(Na^+) = 207.42$ mg/L

No. of additions: 4

Parameters

```
692 pH/Ion Meter            692.0021
date 2001-05-09  time 15:48:59
parameter
  meas.type:        std.add
>measuring parameters
  ion type:         Na(+1)
  conc.unit:        ppm
  meas.input:       1
  electr.id:        0508.100
  drift             0.1 mV/min
  method id         Natrium
  stirrer:          control
  prestir pause     10 s
  stir time         90 s
  poststir pause    20 s
>calculation parameters
  smpl size         40.0 ml
  V total           40.0 ml
  factor            1.0
  smpl size unit:   ml
>standard addition
  type:             add
  conc.std.         207.42 ppm
  report:           full
  addition:         auto
  delta U           12 mV
  dos.rate:         medium
  no.of additions   5
  V Exchange Unit:  10
  activate pulse:   OFF
  stop V            10.0 ml
>preselections
  req.ident:        OFF
  req.smpl size:    value
```

Configuration

```
692 pH/Ion Meter            692.0021
date 2001-05-09  time 15:49:50
config
>printer
  id1        Na ISE/ Polymer
  id2        AB Nr. 83/5
  print header:     always
  calibration report:  OFF
  character set:    Seiko
>print meas.value
  print crit:       immediate
  date&time:        ON
>auxiliaries
  last digit:       ON
  dialog:           english
  date              2001-05-09
  time              15:49:51
  temp.unit:        C
  run number        1
  Dosimat:          665
  device label      692-1
  program           692.0021
>RS232 settings
  baud rate:        9600
  data bit:         7
  stop bit:         1
  parity:           even
  handshake:        HWs
  RS control:       ON
  -------------
```
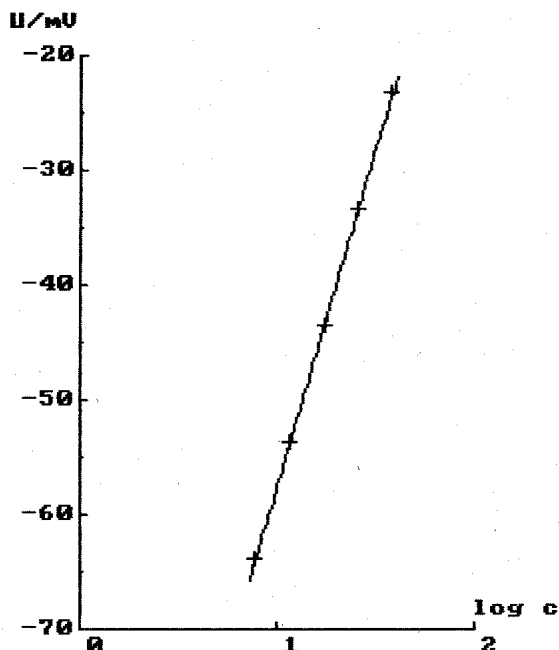
Result

```
692 pH/Ion Meter            692.0021
date 2001-05-21  time 15:14:28   11
Conc     Na4  electr.id    0508.100
id1    Na ISE/ Polymer
id2       AB Nr. 83/5
addition/subtraction method
  meas.type:        std.add
  meas.input:       1
  temperature       24.4  C
  conc.std          207.42 ppm
  V total           40.0 ml
  initial voltage   -64.1 mV
  smpl size         40.0 ml
```

	dV/ml	U/mV	dU/mV
std.incr. 1	0.790	-53.8	10.3
std.incr. 2	1.215	-43.6	10.2
std.incr. 3	1.964	-33.4	10.2
std.incr. 4	3.216	-23.3	10.1

Ω Metrohm

variance   0.000
slope   59.2 mV
E(0)   -116.9 mV
Na(+1)   7.82 ppm

==============

Result of a ninefold determination:

Mean value: 7.83 mg/L Na$^+$

s_{abs}:   0.15 mg/L Na$^+$

s_{rel}:   1.95%

7. Sodium in baby food (milk powder) using automatic standard addition

Electrode:	polymer membrane ISE
Sample preparation:	75.407 g baby food (package information: 0.04 g Na$^+$ / 15 g milk powder; this corresponds to 0.27% Na$^+$) is dissolved in 1 L warm dist. water.
Analysis:	10 mL sample solution and 30 mL dist. water are pipetted into the titration vessel.
Standard:	$\beta(Na^+)$ = 2106.9 mg/L
No. of additions:	5

Parameters

```
692 pH/Ion Meter            692.0021
date 2001-05-10  time  15:11:00
parameter
  meas.type:       std.add
>measuring parameters
  ion type:        Na(+1)
  conc.unit:         ppm
  meas.input:        1
  electr.id:       0508.100
  drift            0.1 mV/min
  method id        Na2
  stirrer:         control
  prestir pause    10 s
  stir time        90 s
  poststir pause   20 s
>calculation parameters
  smpl size        10.0 ml
  V total          40.0 ml
  factor           1.0
  smpl size unit:    ml
>standard addition
  type:            add
  conc.std.        2106.9 ppm
  report:          full
  addition:        auto
  delta U          12 mV
  dos.rate:        medium
  no.of additions   5
  V Exchange Unit:  10
  activate pulse:  OFF
  stop V           10.0 ml
>preselections
  req.ident:       OFF
  req.smpl size:   value
--------------
```

Configuration

```
692 pH/Ion Meter            692.0021
date 2001-05-10  time  15:10:23
config
>printer
  id1      Na ISE/ Polymer
  id2          AB Nr. 83/5
  print header:    always
  calibration report:  OFF
  character set:     Seiko
>print meas.value
  print crit:      immediate
  date&time:         ON
```

Metrohm

>auxiliaries
 last digit: ON
  dialog: english
  date   2001-05-10
  time   15:10:24
  temp.unit: C
  run number   11
  Dosimat: 665
  device label   692-1
  program   692.0021
>RS232 settings
  baud rate: 9600
  data bit: 7
  stop bit: 1
  parity: even
  handshake: HWs
  RS control: ON

Result

692 pH/Ion Meter   692.0021
date 2001-05-10 time 10:04:32   4
Conc   Na2 electr.id   0508.100
id1   Na ISE/ Polymer
id2   AB Nr. 83/5
addition/subtraction method
  meas.type: std.add
  meas.input: 1
  temperature   25.0 C
  conc.std   2106.9 ppm
  V total   40.0 ml
  initial voltage   -48.0 mV
  smpl size   10.0 ml

	dV/ml	U/mV	dU/mV
std.incr. 1	0.371	-37.6	10.4
std.incr. 2	0.562	-27.2	10.4
std.incr. 3	0.863	-16.9	10.3
std.incr. 4	1.374	-6.6	10.3
std.incr. 5	2.292	3.8	10.4
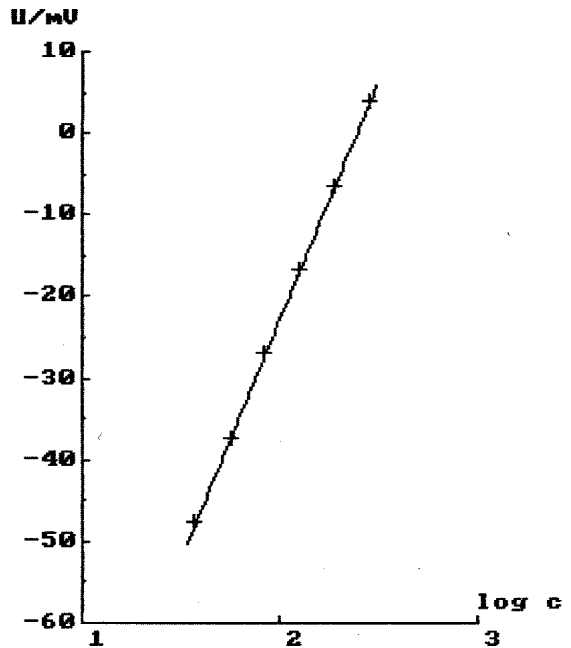
variance	0.005
slope	58.6 mV
E(0)	-140.2 mV
Na(+1)	149 ppm

==============

Result of a tenfold determination:

Sodium concentration in the sample solution:
Mean value: 149.20 mg/L Na^+
S_{abs}:   1.99 mg/L Na^+
S_{rel}:   1.33%

Sodium concentration in the original sample (milk powder):
Mean value: 0.20% Na^+

Ω Metrohm

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