# Application Bulletin

Of interest to: Metals, electroplating A 10

## Potentiometric analysis of anodizing baths


### *Summary*

This bulletin describes potentiometric titration methods for checking sulfuric acid and chromic acid anodizing baths. In addition to the main components aluminum, sulfuric acid and chromic acid, chloride, oxalic acid and sulfate are also determined.


### *Instruments*

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or
  726 or 796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer

The necessary accessories are listed under the different baths.

### *1. Sulfuric acid anodizing bath*

### *Accessories*

- 6.3014.223 Exchange Units (for sodium hydroxide solution possibly with 6.1608.040 reagent bottle made of polyethylene)
- 6.0222.100 combined LL pH glass electrode with 6.2104.020 electrode cable
- 6.0430.100 Ag Titrode with $Ag_2S$ coating
- 6.0431.100 Pt Titrode

### *Reagents*

- Titrant: sodium hydroxide solution, c(NaOH) = 1 mol/L
- Titrant: silver nitrate solution, c($AgNO_3$) = 0.1 mol/L
- Titrant: potassium permanganate solution c($KMnO_4$) = 0.02 mol/L (0.1 N)
- Sulfuric acid, w($H_2SO_4$) = 10%
- Manganese(II) sulfate monohydrate $MnSO_4 * H_2O$, p.a.

## *Analysis*

### *a) Determination of sulfuric acid and aluminum*

Pour approx. 50 mL dist. water into the glass beaker and add 2.0 mL of the anodizing bath sample. Using the combined pH glass electrode titrate with c(NaOH) = 1 mol/L just past the second equivalence point.

#### *Calculation*

The first equivalence point corresponds to the $H_2SO_4$ content, the difference between the second and the first equivalence point to the $Al^{3+}$ content.

1 mL c(NaOH) = 1 mol/L corresponds to 49.04 mg $H_2SO_4$ or 8.994 mg $Al^{3+}$

% $H_2SO_4$ = EP1 * C01 * C03 / C00

% $Al^{3+}$ = (EP2 – EP1) * C02 * C03 / C00

EP1 = titrant consumption to reach the first EP in mL
EP2 = titrant consumption to reach the second EP in mL
C00 = 2.0 (sample volume in mL)
C01 = 49.04
C02 = 8.994
C03 = 0.1 (conversion factor for %)

### *b) Determination of chloride*

Dilute 50.0 mL of the anodizing bath sample with approx. 50 mL dist. water and titrate with c($AgNO_3$) = 0.1 mol/L using the Ag Titrode with $Ag_2S$ coating.

#### *Calculation*

1 mL c($AgNO_3$) = 0.1 mol/L corresponds to 3.545 mg $Cl^-$

% $Cl^-$ = EP1 * C01 * C02 / C00

EP1 = titrant consumption in mL
C00 = 50.0 (sample volume in mL)
C01 = 3.545
C02 = 0.1 (conversion factor for %)

### *c) Determination of oxalic acid*

Pipet 50.0 mL of the anodizing bath sample into the glass beaker, add 10 mL $w(H_2SO_4)$ = 10% and approx. 0.5 g $MnSO_4 * H_2O$ and titrate with $c(KMnO_4)$ = 0.02 mol/L using the Pt Titrode.

***Calculation***

1 mL $c(KMnO_4)$ = 0.02 mol/L corresponds to 4.502 mg oxalic acid

% oxalic acid = EP1 * C01 * C02 / C00

EP1 = titrant consumption in mL
C00 = 50.0 (sample volume in mL)
C01 = 4.502
C02 = 0.1 (conversion factor for %)

## *2. Chromic acid anodizing bath*

## *Accessories*

- 6.3014.223 Exchange Units
- 6.0431.100 Pt Titrode with 6.2104.020 electrode cable
- 6.0430.100 Ag Titrode with $Ag_2S$ coating
- 6.1248.050 W electrode rod with 6.1241.030 electrode shaft and 6.2114.000 electrode cable as well as 6.1248.000 Pt electrode rod with 6.1241.030 electrode shaft and 6.2106.020 electrode cable

## *Reagents*

- Titrant: sodium thiosulfate solution, $c(Na_2S_2O_3)$ = 0.1 mol/L
- Sulfuric acid, $w(H_2SO_4)$ = 96%
- Potassium iodide, p.a.
- Ethanol
- Titrant: silver nitrate solution, $c(AgNO_3)$ = 0.01 mol/L
- Barium chloride solution, $c(BaCl_2)$ = 0.05 mol/L:
  Dissolve 12.214 g $BaCl_2 * 2 H_2O$ in c(HCl) = 0.1 mol/L and make up to 1 L.
- Titrant: c(EGTA) = 0.05 mol/L:
  Dissolve 19.02 g ethylene glycol-bis-(2-aminoethyl)-tetraacetic acid in 250 mL c(NaOH) = 1 mol/L and, after cooling down, make up to 1 L with dist. water.
- Buffer solution pH = 10.5:
  Dissolve 10 g $NH_4Cl$ and 60 mL $w(NH_3)$ = 25% in dist. water and make up to 1 L.
- Strong acidic cation exchanger (e.g. Dowex 50)

## *Analysis*

### *a) Determination of chromic acid*

Pipet 10.0 mL of the anodizing bath sample into a 100 mL volumetric flask, fill to the mark with dist. water and mix thoroughly. Pipet 2.0 mL of this dilution (corresponding to 0.2 mL of the original sample) into a glass beaker, add 40 mL dist. water, 1 mL $w(H_2SO_4)$ = 96% and approx. 1 g potassium iodide and titrate with $c(Na_2S_2O_3)$ = 0.1 mol/L using the Pt Titrode.

#### *Calculation*

1 mL $c(Na_2S_2O_3)$ = 0.1 mol/L corresponds to 3.333 mg $CrO_3$

% $CrO_3$ = EP1 * C01 * C02 / C00

EP1 = titrant consumption in mL
C00 = 0.2 (sample volume used in mL original sample)
C01 = 3.333
C02 = 0.1 (conversion factor for %)

### *b) Determination of chloride*

Pipet 5.0 mL of the anodizing bath sample into a glass beaker. Add 20 mL dist. water, 20 mL ethanol and 1 mL $w(H_2SO_4)$ = 96% and boil for 5 min in order to reduce all Cr(VI) present to Cr(III) (use the fume cupboard!). After cooling down, titrate with $c(AgNO_3)$ = 0.01 mol/L using the Ag Titrode with $Ag_2S$ coating.

#### *Calculation*

1 mL $c(AgNO_3)$ = 0.01 mol/L corresponds to 0.355 mg $Cl^-$ or 0.5844 mg NaCl

mg/L $Cl^-$ = EP1 * C01 * C03 / C00
mg/L NaCl = EP1 * C02 * C03 / C00

EP1 = titrant consumption in mL
C00 = 5.0 (sample volume in mL)
C01 = 0.355
C02 = 0.5844
C03 = 1000 (conversion factor in mL/L)

### *c) Determination of sulfate*

Pipet 1.0 mL of the anodizing bath sample of the bath into a glass beaker. Add 20 mL dist. water, 20 mL ethanol and 1 mL conc. HCl and boil for 5 min in order to reduce all Cr(VI) present to Cr(III) (use the fume cupboard!). After cooling down, percolate through a cation exchanger column into a 100 mL volumetric flask, rinse thoroughly with dist. water, fill to the mark and mix.

Pipet 20 … 50 mL of the prepared bath solution (corresponding to 0.2 … 0.5 mL of the original sample) into a glass beaker, add 5.00 mL $c(BaCl_2)$ = 0,05 mol/L and allow to react for 3 min under stirring. Then add 10 mL buffer solution pH = 10.5 and titrate back the excess of $Ba^{2+}$ with c(EGTA) = 0.05 mol/L using the W and Pt electrode (MET mode).

#### *Calculation*

1 mL c(EGTA) = 0.05 mol/L corresponds to 4.803 mg $SO_4^{2-}$ or 4.904 mg $H_2SO_4$

g/L $SO_4^{2-}$ = (C30 – EP1) *C01 / C00

g/L $H_2SO_4$ = (C30 – EP1) * C02 / C00

EP1 = titrant consumption in mL
C00 = 0.2 ... 0.5 (sample volume used in mL original sample)
C01 = 4.803
C02 = 4.904
C30 = 5.00 [added volume of $c(BaCl_2)$ = 0.05 mol/L in mL]

## *Literature*


- Metrohm Application Bulletin No. 130
  Chloride titrations with potentiometric indication
  Metrohm Ltd., Herisau.
- Metrohm Application Bulletin No. 140
  Analytical determination of sulfate
  Metrohm Ltd., Herisau.
- P. W. Wild
  Moderne Analysen für die Galvanotechnik
  Eugen Leuze Verlag, Saulgau, 1972.

## *Figures*

```
 'fr
785 DMP Titrino          02287   785.0010
user                      th
date  2000-02-07    time  16:32         5
card label:     785
U(init)          322 mV MET U      AB89 a
smpl size       2.00 ml
EP1            4.203 ml             222 mV
EP2            6.995 ml              19 mV
EP3            8.684 ml            -218 mV
H2SO4          10.31 %
Al              1.26 %
stop V reached
          ============
```

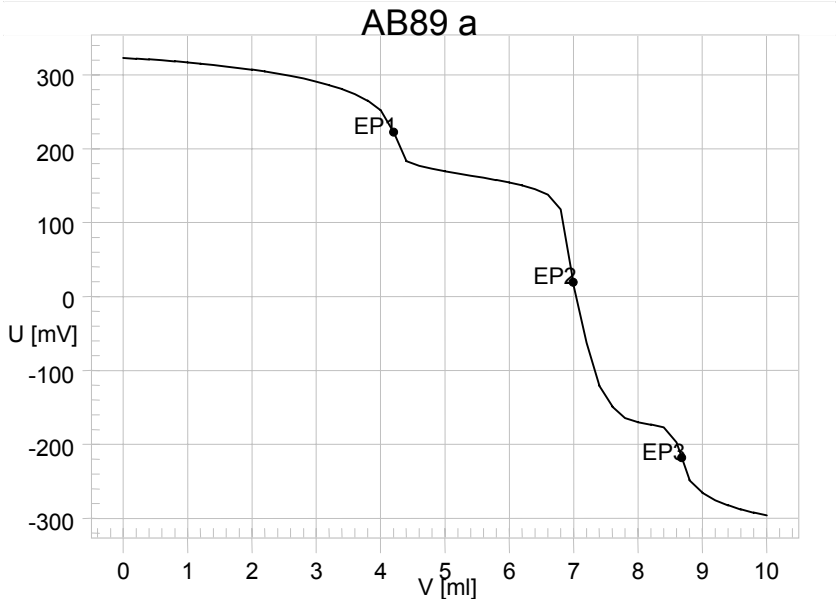


***Fig. 1:*** *Result block and titration curve for the determination of sulfuric acid and aluminum in an anodizing bath.*

```
 'pa
785 DMP Titrino          02287   785.0010
user                    th
date  2000-02-08    time  09:29         6
MET  U                AB89 c
parameters
>titration parameters
  V step                   0.1 ml
  dos.rate                max. ml/min
  signal drift              40 mV/min
  equilibr.time             28 s
  start V:                 OFF
  pause                     30 s
  meas.input:                1
  temperature              25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                     3 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       30 mV
  EP recognition:    greatest
  fix EP1 at U             OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  limit smpl size:         OFF
  activate pulse:          OFF
          ============
```

***Fig. 2:*** *Parameter settings for the determination of oxalic acid.*

```
 'fr
785 DMP Titrino          02287   785.0010
user                    th
date  2000-02-08    time  09:29         6
card label:     785
U(init)         -134 mV MET U       AB89 c
smpl size       50.0 ml
EP1            1.762 ml            -563 mV
Oxalic a      0.0159 %
stop V reached
          ============
```

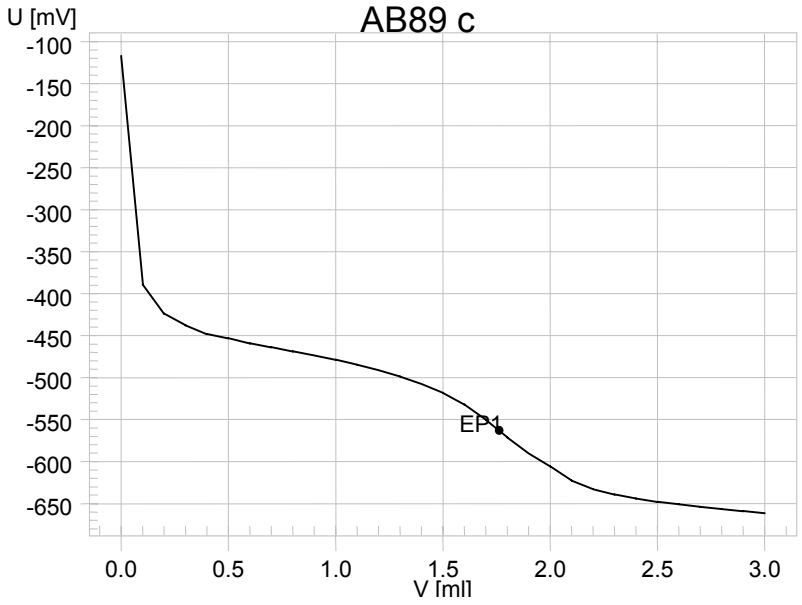


***Fig. 3:*** *Result block and titration curve for the determination of oxalic acid in an anodizing bath.*

```
 'pa
785 DMP Titrino          02287   785.0010
user                    th
date  2000-02-08    time  11:46       13
MET  U                 AB89 A
parameters
>titration parameters
  V step                   0.1 ml
  dos.rate                max. ml/min
  signal drift              30 mV/min
  equilibr.time             32 s
  start V:                 OFF
  pause                     0 s
  meas.input:               1
  temperature              25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    11 ml
  stop U                   OFF mV
  stop EP                   9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       30 mV
  EP recognition:    greatest
  fix EP1 at U             OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  limit smpl size:         OFF
  activate pulse:          OFF
          ============
```

***Fig. 4:*** *Parameter settings for the determination of chromic acid.*

```
 'fr
785 DMP Titrino          02287   785.0010
user                    th
date  2000-02-08    time  11:46       13
card label:     785
U(init)           9 mV MET U      AB89 A
smpl size      0.20 ml
EP1           8.883 ml             159 mV
CrO3          14.80 %
stop V reached
          ============
```

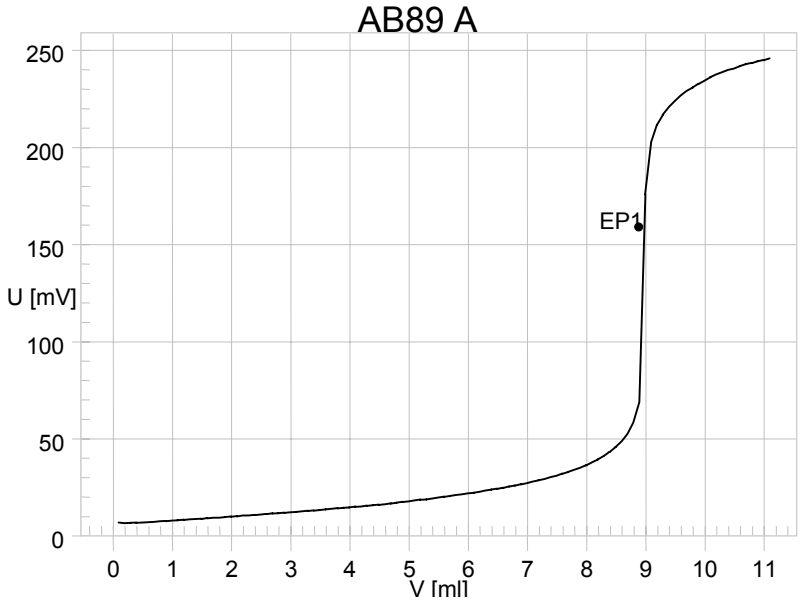


***Fig. 5:*** *Result block and titration curve for the determination of chromic acid in an anodizing bath.*

```
 'pa
785 DMP Titrino          02287   785.0010
user                    th
date  2000-02-09    time  14:29         7
MET  U                AB89 C
parameters
>titration parameters
  V step                  0.05 ml
  dos.rate                max. ml/min
  signal drift              50 mV/min
  equilibr.time             26 s
  start V:                 OFF
  pause                     30 s
  meas.input:                1
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                     6 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       10 mV
  EP recognition:    greatest
  fix EP1 at U             OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  limit smpl size:         OFF
  activate pulse:          OFF
          ============
```

***Fig. 6:*** *Parameter settings for the determination of sulfate.*

```
 'fr
785 DMP Titrino          02287   785.0010
user                    th
date  2000-02-09    time  14:29         7
card label:     785
U(init)         380 mV MET U      AB89 C
smpl size       0.2 ml
EP1           4.846 ml             397 mV
SO4 2-         9.99 g/l
H2SO4         10.20 g/l
stop V reached
          ============
```

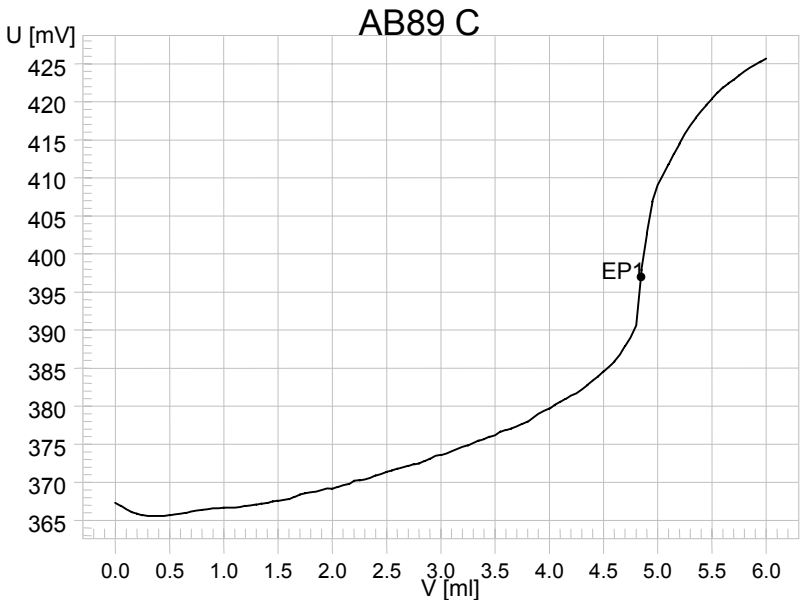


***Fig. 7:*** *Result block and titration curve for the determination of sulfate in an anodizing bath.*