

# Application Bulletin

Of interest to: Metallurgy, electroplating

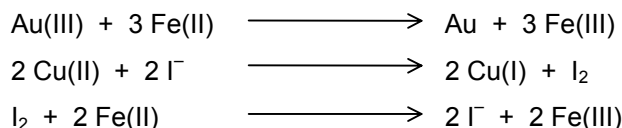
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## Simultaneous determination of gold and copper in electroplating baths and/or alloys by potentiometric titration

### Summary

This bulletin describes the simultaneous determination of gold and copper by potentiometric titration using an Fe(II) solution as titrant. Fe(II) reduces Au(III) directly to the free metal, whereas Cu(II) does not react. By the addition of fluoride ions the Fe(III) is complexed and a shift of the redox potential is effected. Afterwards, potassium iodide is added, thus reducing the Cu(II) to Cu(I), and the free iodine is again titrated with the Fe(II) solution using a Pt Titrode.

#### Chemical reactions:



### Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 Titroprocessor with 685 Dosimat or 700 Dosino
- 2.728.0040 Magnetic Stirrer
- 6.3014.213 Exchange Unit 10 mL (with flat PCTFE/PTFE stopcock)
- 6.0431.100 Pt Titrode with 6.2104.020 electrode cable
- Possibly printer and printer cable

### Reagents

- Titrant: Fe(II) solution,  $c(\text{Fe}^{2+}) = 0.1 \text{ mol/L}$ :  
In a 500 mL volumetric flask, add 5 mL concentrated HCl to 20 g  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ , dissolve in dist. water and fill to the mark.  
For the titer determination the Cu(II) solution mentioned below is used.
- Cu(II) solution,  $c(\text{Cu}^{2+}) = 0.05 \text{ mol/L}$ :  
In a 500 mL volumetric flask, dissolve 6.242 g  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  in dist. water, add 2.5 mL concentrated  $\text{H}_2\text{SO}_4$  and fill to the mark with dist. water.

- Acetate buffer pH = 4.64:  
Dissolve 50 g sodium acetate and 3 mL concentrated acetic acid in dist. water and make up to 250 mL.
- Potassium fluoride solution:  
Dissolve 100 g potassium fluoride in dist. water and make up to 500 mL. Store the solution in a plastic bottle.
- Potassium iodide solution:  
Dissolve 3.32 g potassium iodide in dist. water and make up to 100 mL. Store the solution in a dark bottle.
- Concentrated HCl and concentrated HNO<sub>3</sub>

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### **Sample preparation**

In a 100 mL glass beaker, carefully mix 10 mL of the plating bath sample with 10 mL concentrated HCl and heat up (Caution! HCN fumes will escape, therefore use the fume cupboard!). Afterwards, boil down, allowing approx. half to evaporate, then add concentrated HNO<sub>3</sub> drop by drop (0.5 mL at most) until all the precipitated gold has redissolved. Now boil again and evaporate down to half the volume, allow to cool, then fill to the mark with dist. water in a 50 mL volumetric flask.

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### **Analysis**

#### **Determination of gold**

Add 30 mL acetate buffer to 10.0 mL of the prepared sample solution (this corresponds to 2 mL of the original sample) in a glass beaker and titrate with the Fe(II) solution.

#### **Determination of copper**

This is carried out directly after the Au determination. Add 5 mL potassium fluoride solution as well as 10 mL potassium iodide solution to the sample, then titrate again with the Fe(II) solution.

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### **Calculation**

1 mL c(Fe<sup>2+</sup>) = 0.1 mol/L corresponds to 6.566 mg Au or 6.355 mg Cu

$$\text{g/L Au} = \text{EP1} * \text{C01} * \text{C02} / \text{C00}$$

$$\text{g/L Cu} = \text{EP1} * \text{C01} * \text{C03} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = 2 (sample volume used in mL original sample)

C01 = titer of the titrant

C02 = 6.566 (equivalent weight Au in mg/mL)

C03 = 6.355 (equivalent weight Cu in mg/mL)

### Remark

The method is, of course, also suitable for the determination of the two metals in alloys after prior digestion. Make sure that the  $\text{HNO}_3$  is completely evaporated as this would interfere with the subsequent determinations.

### Figures

```
'pa
716 DMS Titrino      OE2/239  716.0020
date 99-04-28      time 09:47    14
DET U              *****
parameters
>titration parameters
  meas.pt.density      4
  min.incr.           10.0 µl
  titr.rate            max. ml/min
  signal drift        50 mV/min
  equilibr.time       26 s
  start V:            OFF
  pause               0 s
  meas.input:         1
  temperature         22.4 °C
>stop conditions
  stop V:             abs.
  stop V              5 ml
  stop U              OFF mV
  stop EP             9
  filling rate        max. ml/min
>statistic
  status:             OFF
>evaluation
  EPC                 5
  EP recognition:     greatest
  fix-EP1 at U       OFF mV
  pK/HNP:            OFF
>preselections
  req.ident:         OFF
  req.smpl size:     OFF
  activate puls:     OFF
  =====
```

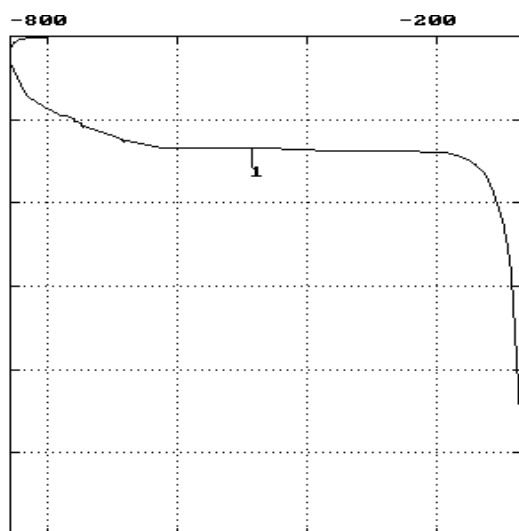
**Fig. 1:** Parameter settings on the 716 DMS Titrino.

```
'fr
716 DMS Titrino      OE2/239  716.0020
date 99-04-28      time 09:56  15
U(init)            -661 mV  DET U  *****
simpl size         2 ml
EPl                1.359 ml  -486 mV
Au                 3.461 g/l
stop V reached
=====
```

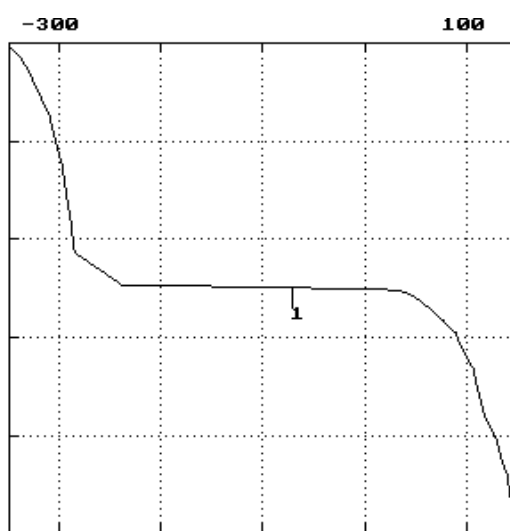
```
'fr
716 DMS Titrino      OE2/239  716.0020
date 99-04-28      time 11:07  17
U(init)            -348 mV  DET U  *****
simpl size         2 ml
EPl                2.495 ml  -70 mV
Cu                 5.336 g/l
stop V reached
=====
```

```
'cu
716 DMS Titrino      OE2/239  716.0020
date 99-04-28      time 09:56  15
start V            0.0000 ml  DET U  *****
1.0 ml/div        dU=200.0 mV/div
```

```
'cu
716 DMS Titrino      OE2/239  716.0020
date 99-04-28      time 11:07  17
start V            0.0000 ml  DET U  *****
1.0 ml/div        dU=100.0 mV/div
```



**Fig. 2:** Result block and titration curve for a Au determination.



**Fig. 3:** Result block and titration curve for a Cu determination.

## Literature

- C. Mahr, B. Seeger  
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- S. K. Cirkov, V. S. Romanova  
Eine elektrometrische Methode ohne Kompensation zur Goldbestimmung mit Mohr'scher Salzlösung  
Zh. Anal. Khim. 14 (1959) 198–201 (in Russian)  
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- S. Wolf  
Die Bestimmung von Gold und Kupfer in galvanischen Bädern durch potentiometrische Titration  
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