DA 135 A 265 : MANCANTI

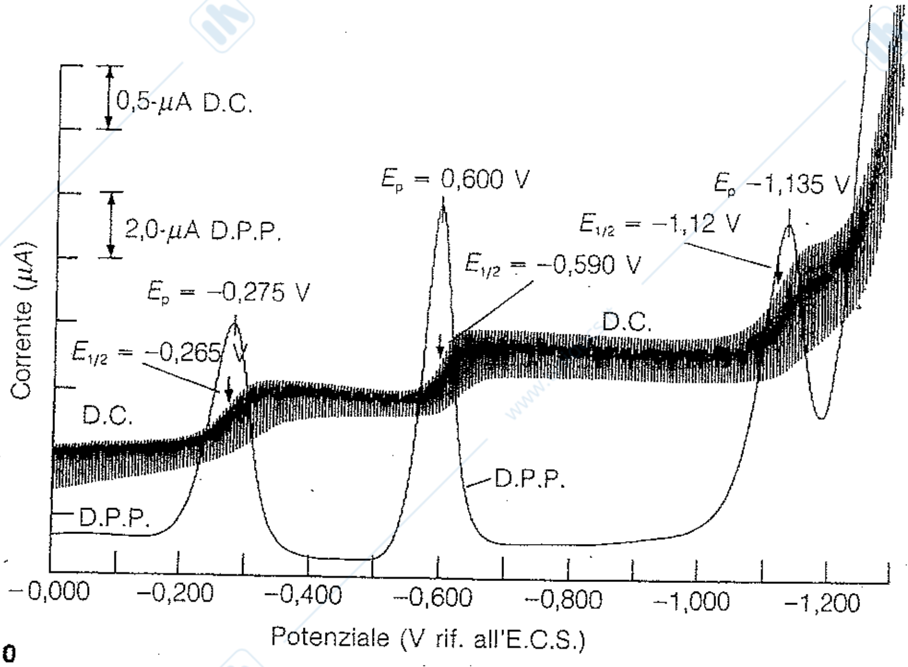


Figura 19.10

Confronto tra polarografia a corrente continua (D.C.) e polarografia differenziale a impulsi (D.P.P.) del clorodiazoepossido (il farmaco Librium) 1,2 · 10^{-4} M in 3 mL di H_2SO_4 0,05 M. Ampiezza di modulazione = 50 V. Notare le diverse scale di corrente per ciascuna curva. [M.R. Hackman, M.A. Brooks, J.A.F. de Silva e T.S. Ma, *Anal. Chem.*, **46**, 1075 (1974)]. Si ritiene che i processi responsabili di ciascun onda siano quelli sotto rappresentati. [E. Jacobsen e T.V. Jacobsen, *Anal. Chim. Acta*, **55**, 293 (1971)].

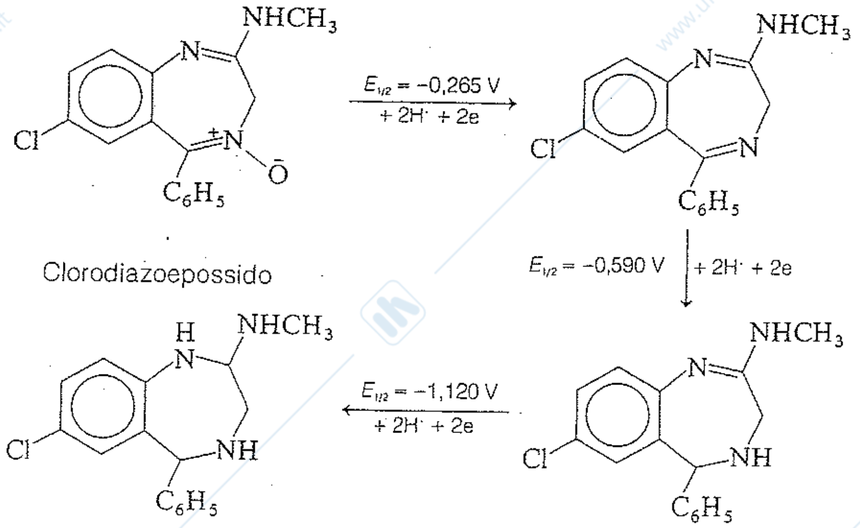
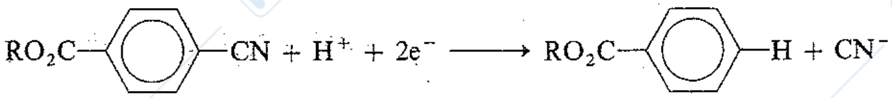
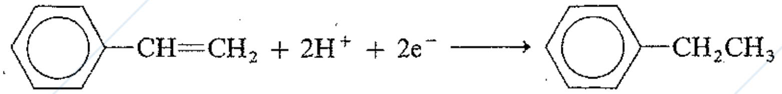
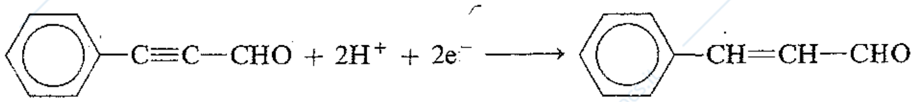
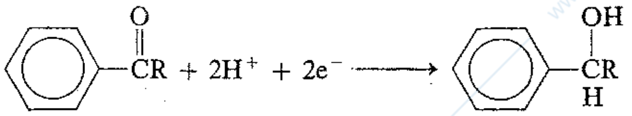
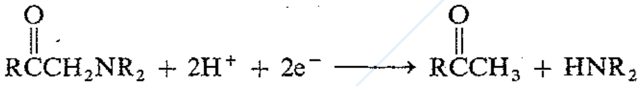
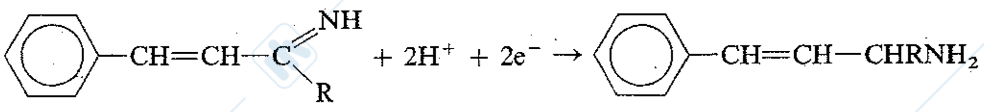
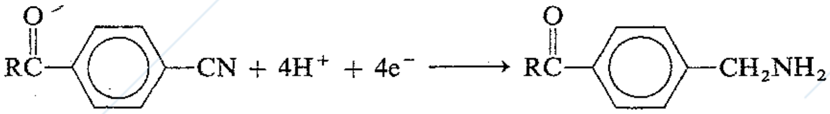
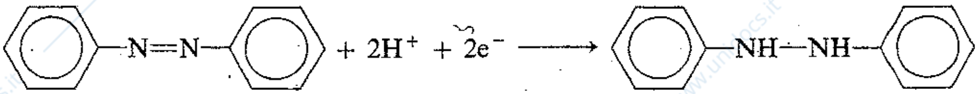


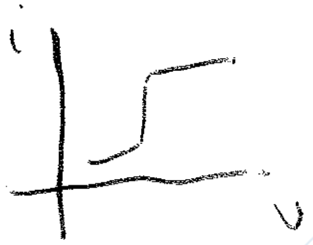
Tabella 19.4

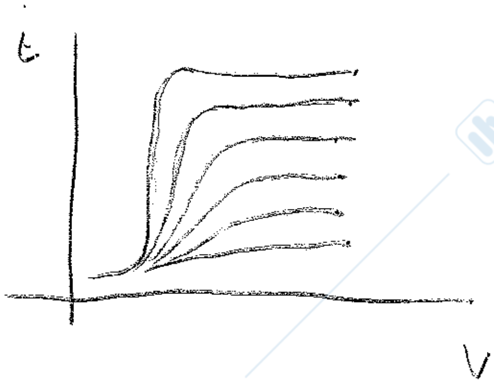
Comportamento polarografico di alcuni gruppi funzionali

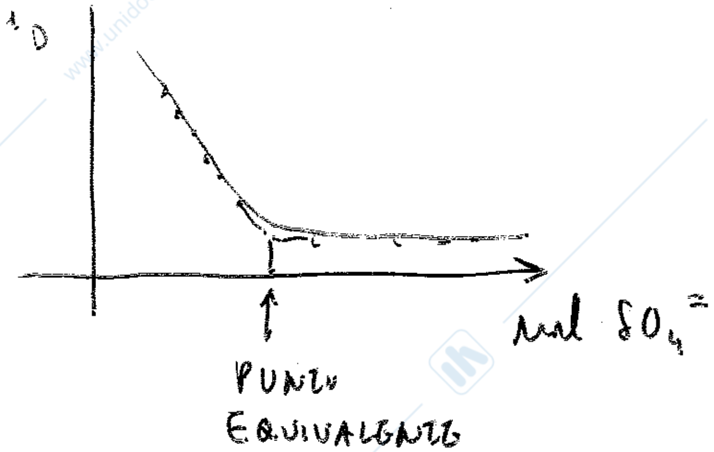
Gruppo	Reazione
C—C	
C═C	
C≡C	
C—X	$RCH_2Br + H^+ + e^- \rightarrow RCH_3 + Br^-$
C═O	
C—N	 $R\overset{\overset{O}{\parallel}}{C}CH_2NR_2 + 2H^+ + 2e^- \longrightarrow R\overset{\overset{O}{\parallel}}{C}CH_3 + HNR_2$
C═N	
C≡N	
N═N	
N═O	$R{-}NO + 2H^+ + 2e^- \rightarrow RNHOH$
NO_2	$RNO_2 + 4H^+ + 4e^- \rightarrow RNHOH + H_2O$
O—O	$ROOR + 2H^+ + 2e^- \rightarrow 2ROH$
S—S	$RSSR + 2H^+ + 2e^- \rightarrow 2RSH$
S═O	$R_2S{=}O + 2H^+ + 2e^- \rightarrow R_2S + H_2O$

TITOLAZIONI AMPEROMETRICHE

ESEMPIO Pb^{2+} PRECIPITATO CON $SO_4^{=}$



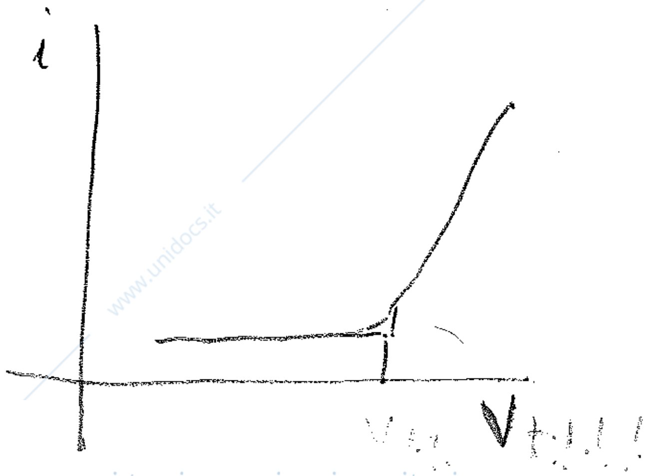




SE AVESSIMO TITOLATO CON $Cr_2O_7^{=}$ → $PbCrO_4$

$$Cr_2O_7^{=} + 6e^- + 14H^+ \rightarrow 2Cr^{+3} + 7H_2$$

SE SOLO IL TITOLANTE FOSSE STATO ELETTROATTIVO



TITOLAZIONI BIAMPEROMETRICHE (DEAD STOP)

INCROCIO FRA POTENZIOMETRIA E VOLTAMMETRIA

DUE ELETTRODI POLARIZZABILI FRA I QUALI VIENE APPLICATA UNA DIFFERENZA DI POTENZIALE DI 100 mV (DUE FILI DI PLATINO, UNO FUNGE DA CATODO, L'ALTRO DA ANODO)

LA SOLUZIONE E' AGITATA

E' NECESSARIO CHE IL TITOLANTE O L'ANALITA O ENTRAMBI FACCIANO PARTE DI UNA COPPIA RED-OX REVERSIBILE

ESEMPIO TITOLAZIONE DI Fe^{+2} CON Ce^{+4}

$$Fe^{+2} + Ce^{+4} \longrightarrow Fe^{+3} + Ce^{+3}$$

ALL'INIZIO $I = 0$ PERCHE' Fe^{+2} POTREBBE OSSIDARSI MA NESSUNA RIDUZIONE E' POSSIBILE

DOPO L'AGGIUNTA DI UN PO' DI Ce^{+4} IN SOLUZIONE SONO PRESENTI Fe^{+2} Fe^{+3} Ce^{+3}

ALL'ANODO $Fe^{+2} \rightarrow Fe^{+3} + e^-$

AL CATODO $Fe^{+3} + e^- \rightarrow Fe^{+2}$

Fe^{+2} POTREBBE FORNIRE CORRENTE MAGGIORE MA NON PUO' PERCHE' NON C'E' SUFFICIENTE Fe^{+3}

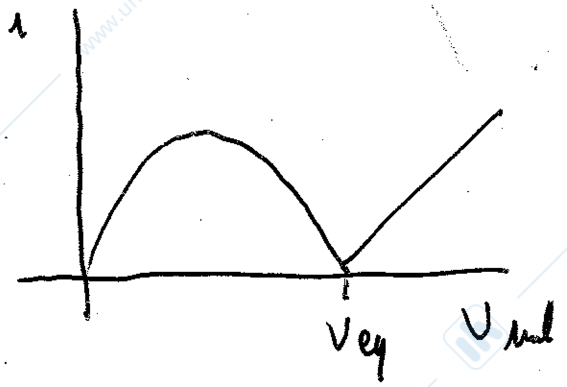
$$i_{ANODICA} = i_{CATODICA}$$

LA CORRENTE E' MASSIMA QUANDO $[Fe^{+2}] = [Fe^{+3}]$ (METÀ TITOLAZIONE) E POI INIZIA A DIMINUIRE FINO A ZERO (PUNTO EQUIVALENTE) PERCHÉ SONO PRESENTI SOLO Fe^{+3} e Ce^{+3}

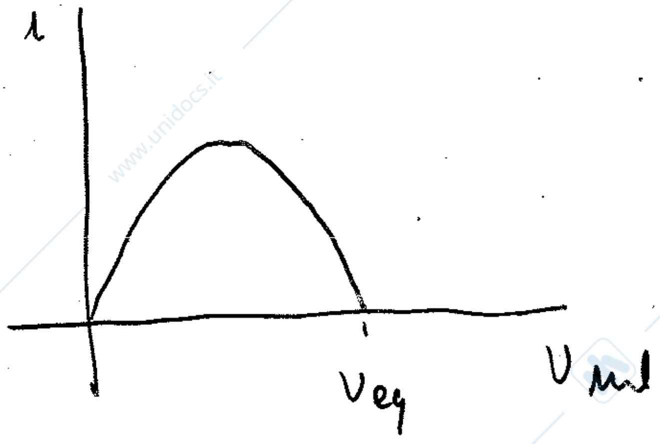
AL PRIMO ECCESSO DI Ce^{+4}

ALL'ANODO $Ce^{+3} \rightarrow Ce^{+4} + e^-$

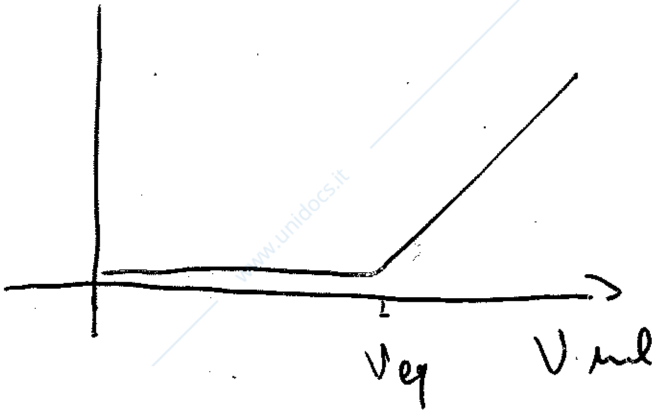
AL CATODO $Ce^{+4} + e^- \rightarrow Ce^{+3}$ $\qquad I_{CAT} = I_{AN}$



ALTRI ESEMPI:



SOLO L'ANALITA APPARTIENE A UNA COPPIA REDOX



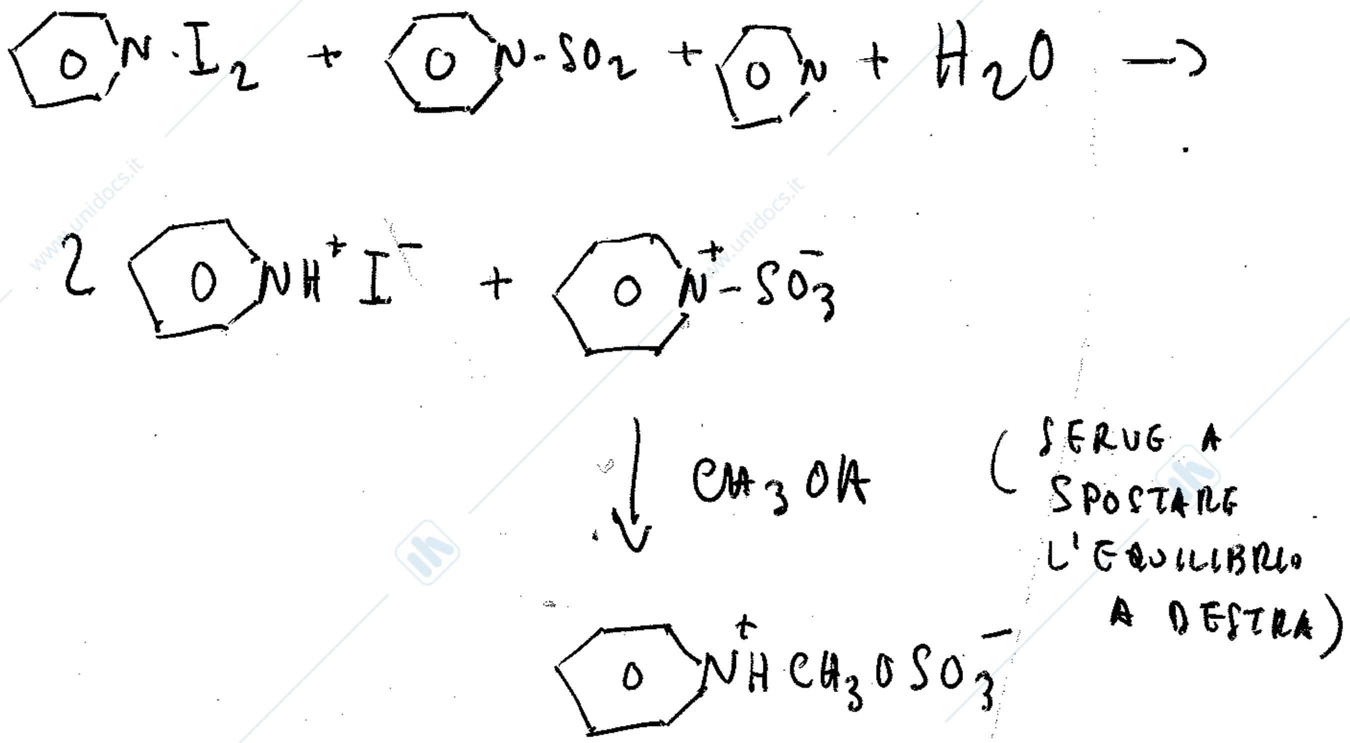
SOLO IL TITOLANTE APPARTIENE A UNA COPPIA REDOX

LA COPPIA I_2/I^- PUO' ESSERE UTILIZZATA AD ESEMPIO

DETERMINAZIONE DI H_2O KARL FISCHER

REATTIVO KF I_2 PIRIDINA SO_2 1:10:0.3

IN METANOLO O ALTRO SOLVENTE



(SERVE A SPOSTARE L'EQUILIBRIO A DESTRA)

SI TITOLA UN VOLUME NOTO DI REATTIVO STANDARDIZZATO CON H_2O/CH_3OH STANDARD CON UNA SOLUZIONE DEL CAMPIONE

DEAD STOP (SOLO ANALITA ELETTROATTIVO)

VARIANTE BIPOTENZIOMETRICA

CORRENTE COSTANTE FRA DUE ELETTRODI (10 µA) E SI SEGUE IL POTENZIALE (CON POTENZIOMETRO/PIACCAMETRO)

SI TITOLA CON IL REATTIVO

PRIMA DEL PUNTO EQUIVALENTE C'E' SOLO I^-

E SERVE UN POTENZIALE ELEVATO PER MANTENERE LA CORRENTE

AL PUNTO EQUIVALENTE V CROLLA PER LA PRESENZA DI I_2

32a S

1 The Karl Fischer reaction

The determination of the water content is based on the reaction described by R. W. Bunsen [1]:

$$I_2 + SO_2 + 2\,H_2O \longrightarrow 2\,HI + H_2SO_4$$

Karl Fischer [2] discovered that this reaction could be used for water determinations in a non-aqueous system containing an excess of sulfur dioxide. Methanol proved to be suitable as a solvent. In order to achieve an equilibrium shift to the right, it is necessary to neutralize the acids that are formed during the process (HI and H_2SO_4). Karl Fischer used pyridine for this purpose.
Smith, Bryanz and Mitchell [3] formulated a two-step reaction:

$$I_2 + SO_2 + 3\,Py + H_2O \longrightarrow 2\,Py\text{-}H^+I^- + Py{\bullet}SO_3$$
$$Py{\bullet}SO_3 + CH_3OH \longrightarrow Py\text{-}H^+CH_3SO_4^-$$

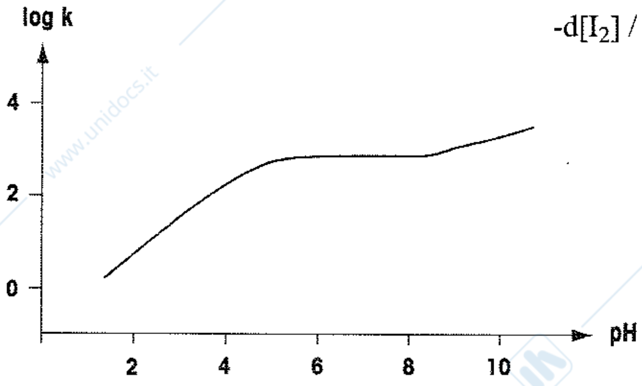
According to these equations, methanol not only acts as a solvent but also participates directly in the reaction itself. In an alcoholic solution, the reaction between iodine and water takes place in the stoichiometric ratio of 1:1.
In an alcohol-free solution, the reaction between iodine and water takes place in the stoichiometric ratio of 1:2:

$$I_2 + SO_2 + 3\,Py + \mathbf{H_2O} \longrightarrow 2\,Py\text{-}H^+I^- + Py{\bullet}SO_3$$
$$Py{\bullet}SO_3 + \mathbf{H_2O} \longrightarrow Py\text{-}H^+HSO_4^-$$

Further studies conducted by E. Barenrecht and J. C. Verhoff [4] on the subject of the Karl Fischer reaction have revealed that

- Pyridine is not directly involved in the reaction, i.e., it only acts as a buffering agent and can therefore be replaced by other bases,
- the rate of the Karl Fischer reaction depends on the pH value of the medium (see graph):

$$-d[I_2] / dt = k\,[I_2] \bullet [SO_2] \bullet [H_2O]$$



One explanation for this relationship between the pH value and the reaction rate is that it is not the sulfur dioxide itself that is oxidized by iodine under the influence of water, but rather the methyl sulfite ion, which is formed from sulfur dioxide and methanol:

$$2\,CH_3OH + SO_2 \longrightarrow CH_3OH_2^+ + CH_3OSO_2^-$$

The higher the pH value of the solution, the more methyl sulfite is formed by the capture of protons and the faster the Karl Fischer reaction.

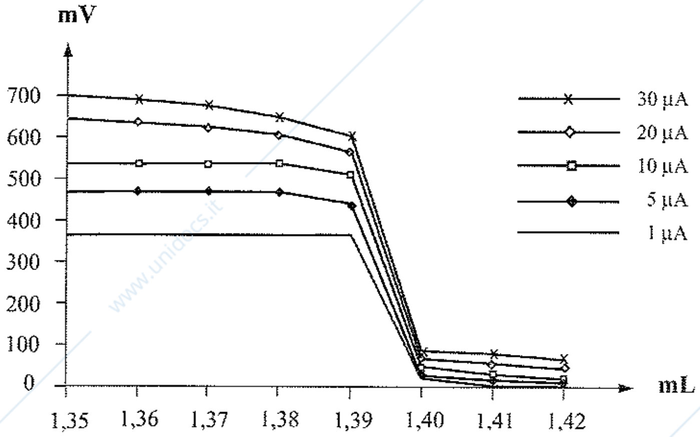
32bS

3.1.2 End point and polarization current

The Karl Fischer titration is terminated when free iodine is detected in the titration solution, i.e., the titration end point is reached when the potential at the polarized, double platinum pin electrode drops below a defined value. This value depends, above all, on the polarization current and to a lesser extent on the type of electrode as well as on the solvent that is used.

The following end points have been defined for reagents containing methanol (with double platinum pin electrode, pin length: 3 to 4 mm, pin diameter: 1 mm):

Ipol	End point
1 µA	20 to 30 mV
5 µA	50 to 70 mV
10 µA	80 to 100 mV
20 µA	100 to 120 mV
30 µA	130 to 150 mV
40 µA	150 to 170 mV



Notes

1. You can use the same end points for ethanol-based reagents.
2. You should use end points roughly 20% higher for reagents for aldehydes and ketones, where the methanol has been replaced by 2-methoxyethanol.

Influence of the electrode

The potential jump at the end of the titration is also influenced by the electrode:

- Electrodes with a large platinum surface, e.g. with longer pins, a double ring or plates instead of pins, result in a smaller potential jump and a lower end point. The larger the platinum surface, the smaller the potential jump. Double-ring electrodes, for example, have an initial potential of approx. 350 mV and an end point at approx. 40 mV with 20 µA.
- Electrodes with very short platinum pins (< 3 mm), on the other hand, cause a larger potential jump and a higher end point. A 2 mm long pin, for example, causes an initial potential of approx. 750 mV and an end point at approx. 140 mV with 20 µA.

3.2 Reaction rate

The reaction rate depends on

- the water concentration,
- the sulfur dioxide concentration,
- the iodine concentration,
- the pH value of the solution (see Section 1).