Pure & Appl. Chem., Vol. 56, No. 8, pp. 1095–1129, 1984.
Printed in Great Britain.

0033-4545/84 $3.00+0.00
Pergamon Press Ltd.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

VOLTAMMETRY AT GLASSY CARBON ELECTRODES

Prepared for publication by

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VOLTAMMETRY

at

GLASSY CARBON ELECTRODES

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Abstract :

Recommended pretreatment procedures are described for obtaining reproducible and accurate results. Based on a worldwide survey, information is tabulated on the working range of potentials of glassy carbon in water, organic solvents, and molten salts. Voltammetric characteristics of numerous redox couples are documented.

Contents :

The present report is intended to describe and to recommend specific treatments in the preparation of glassy carbon (G.C.) as an electrode material.

The information summarized in this report illustrates the unique capabilities of glassy carbon electrodes with respect to other electrode materials. G.C. electrodes may be employed to obtain accurate and reproducible results on a large variety of redox systems and in a wide range of solvents. However, this goal can be achieved only if the G.C. electrode receives the proper pretreatment and is then handled appropriately.

Chemically modified glassy carbon electrodes, especially Hg-plated glassy carbon electrodes (thin film mercury electrodes, MFE), while important in ultra-trace analytical chemistry, are not reviewed in the present report. Specific papers have been published on analytical applications of such electrodes. (L. Mart, H.W. Nürnberg, P. Valenta, Fresenius Z. Anal. Chem., 300, 350-362 (1980)).

I. THE STARTING MATERIALS

Nine different commercial sources of G.C. were identified and are listed in Appendix A.

The first paper published on G.C. was by Sh. Yamada and H. Sato (Nature, 193 (4812), p.261 (1962)).

II. PREPARING THE G.C. ELECTRODE SURFACE FOR ELECTROCHEMICAL MEASUREMENTS

Careful checking of answers to an ad hoc questionnaire (see VI below) and of the published literature leads to the conclusion that many different procedures have been used by various investigators.

However the following general trends emerge from intercomparison of these procedures, as necessary steps to warrant good reproducibility of the electrochemical results.

1. Physical treatment

Two successive steps are usually involved in the polishing of the G.C. surface

Abrasion with emery paper of increasing fineness (typically 240, 320, 400 and 600 mesh per sq.i. or 32, 23, 15, 8, 5, 3, 1 μm SiC , 2 min. each).

Polishing with water (alumina or chromium III oxide) or oil (diamond) suspensions with decreasing particle size (typically from 5 - 10 to 0.5 μm or 0.25 μm).

It is critical to rinse carefully the surface of the electrode (with water or another solvent) between two polishing steps.

Some authors (5) (20) (28) recommend to use ultrasonic vibrations to clean the surface (dislodging impurities held in pores at the surface). Typical solvents are : hexane, acetone, water. Few minutes each.
Also it was observed (39) (42) that vacuum desorption under 1 torr or less, at normal (42) or high (500°C) temperatures (39), increases the reproducibility of the results (39) (42) and the reversibility (42) of the electrode reactions.

Specially relevant to this question is the recent study (44) of the relationship between the heat treatment temperature of G.C. and the kinetic parameters of various redox reactions. This question was also discussed in previous papers (39) (41).

2. Chemical pretreatment

Depending on the intended use of the G.C., specific chemical pretreatments may be added to the physical treatment.

- to obtain an electrode surface free of oxygen containing groups :
surface treatments with non oxidizing acids (HCl for instance) (48) in solution free of oxidizing species ; polarization of the electrode at a potential slightly negative to SCE.

- to obtain an electrode surface free of adsorbed species :
wash the electrode with ethanol or chloroform, then wipe the surface with a wet filter paper.

3. Electrochemical pretreatment

The purpose of this pretreatment is to increase the rate of the electron transfer steps at the electrode surface and also to warrant reasonable reproducibility of the experimental results. Several authors made extensive use of electrochemical pretreatments of G.C. electrodes (4) (14) (15) (19) (21) (23) (25) (32) (33) (37) (40) (43 (45). The practice has also been reviewed critically (41) (44).

This pretreatment involves applications of several "polarization cycles" to the electrode, in order to obtain a specified reproducible "surface condition".

However, the potential limits of the cycles have to be set far enough from zero volt (versus SCE), in order for the activation to occur.

As a general rule, the activation of the G.C. electrode surface occurs when the potential is cycled at intermediate scan rates (typically 0.1 V/s) between moderately negative potentials (i.e. about - 0.5 V) and more positive potentials, viz. + 0.9 to + 1.50 V/SCE (37) (40) (43) (44) (45). It should be noted that such "activated electrodes" exhibit improved reproducibility and reversibility, at the expense of the analytical sensitivity. The latter is handicapped by enhancement of residual currents (14) (44) (50).

It should also be kept in mind that the G.C. electrode is irreversibly damaged at too positive potentials (>2 Volts/SCE) and by high anodic currents (>100 mA) (12).

III. GEOMETRIC CHARACTERISTICS OF THE G.C. ELECTRODES

When used for analytical purposes, the preferred geometry is a circular cross-section of a cylindrical rod of small area, whereas other geometries are involved in preparative electrolysis, which requires large effective areas (e.g. plates (52), reticulated vitreous carbon (32)).

"Rod cross section" electrodes are usually prepared by inserting rod-shaped electrodes (commercial diameters range typically from 3 to 8 mm), of about 10 mm in length, into tubes of teflon, or plexiglass, or pyrex, and by sealing the rod to the tube with epoxy (for instance Epo-Tek 349, Epoxy Technology, Watertown, Mass).

However, it is preferable to use rod electrodes inserted in tight-fitting teflon tubes, in order to avoid contamination of ambient electrolytes by epoxy.

Typically, fitting is achieved by "forcing" the carbon rod into a teflon sheath whose inner (bore) diameter is about 15 % smaller than the rod.

Electrical contact with the electrode is made via the top of the carbon rod with the aid of silver epoxy or mercury.

IV. ELECTROACTIVITY RANGE OF THE G.C. ELECTRODE

The electroactivity range of G.C. is remarkably large in a wide variety of solvents, as documented in Appendix B. A working range of 3 Volts is common.

However, it should be noted that the electroactivity range of G.C. electrodes is dependent on the prevailing "surface condition" (41,44).

V. REDOX SYSTEMS STUDIED ON G.C. ELECTRODES

are listed in Appendix C and include the following couples.

(1) Ferrocene/Ferricinium
(2) $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$

} : Table (1)

(store solutions of $Fe(CN)_6^{4-}$ in the dark, to avoid photodegradation).

(3) Other redox systems : Table (2)

VI. IDENTIFICATION OF THE SOURCES QUOTED IN THIS REPORT

Two types of source materials were used :

a) answers to a questionnaire distributed to 332 prominent electrochemists worldwide. Forty seven (47) responses were received.

b) published papers.

Each source has been assigned a code number and is identified accordingly, both in the foregoing text and in the following tabulations. The code numbers are listed in Appendix D.

VII. TABLE OF ABBREVIATIONS AND SYMBOLS

ACV	Alternating Current Voltammetry
AN	Acetonitrile
ASV	Anodic Stripping Voltammetry
BN	Benzonitrile
CA	Chronoamperometry
CV	Cyclic Voltammetry
DCP	Direct Current Polarography
DMF	Dimethylformamide
DPP	Differential Pulse Polarography
DPV	Differential Pulse Voltammetry
El	Electrolysis
$E_{1/2}$	Halfwave potential
E_{pa}	Potential of anodic peak in C V
E_{pc}	Potential of cathodic peak in C V
Fc/Fc^{+}	Ferrocene/Ferricinium
GC	Glassy Carbon
GCE	Glassy Carbon Electrode
HYV	Hydrodynamic Voltammetry
IRREV	Irreversible
LSV	Linear scanning voltammetry
M	Mole . litre -1
Me_2SO	Dimethylsulfoxide
n-PrCN	n-propionitrile
NHE	Normal Hydrogen Electrode
NPP	Normal Pulse Polarography
PC	Propylene Carbonate
Pot	Potentiometry
PY	Direct current polarography
QRev	Quasi reversible
Rev	Reversible
RDE	Rotating disk electrode
RDEV	Voltammetry on Rotating disk electrode
SCE	Calomel Electrode in KCl Saturated solution
SHE	Standard Hydrogen Electrode
SR	Scan Rate
SSCE	Calomel Electrode in NaCl satured solution
TBAP	Tetra-n-butyl-ammonium perchlorate
$TBAPF_6$	Tetrabutyl ammonium hexafluorophosphate
TEAP	Tetraethyl ammonium perchlorate
TEAPTS	Tetraethyl ammonium para-toluene sulfonyl
THAP	Tetrahexyl ammonium perchlorate
THF	Tetrahydrofuran
TMAP	Tetramethyl ammonium perchlorate

APPENDIX A : STARTING MATERIALS

(1) Le Carbone Lorraine, Département Produits Spéciaux, 37 à 41, rue Jean Jaurès, F-92230 Gennevilliers (France), Télex F-620847 LCLGV, Tel. (1) 799.98.41.

(2) China Scientific Instruments and Materials Corporation, 75, W. Dengshi Street, Beijing (China), Cable adress : "CSIMC" Beijing.

(3) Fluorocarbon Company, Process Systems Division, 1432 So. Allec St., Anaheim, California, 92803 (USA), Tel. 714/956-7330.

(4) Tokai Carbon Co/IMC Industry Group & Associates, Ming-Yu International Building, 8-8, 4-chome Ginza, Chuo-Ku, Tokyo 104 (Japon), Telex J-22 316, J-22 923, Tel. (535) 4381.

*(5) Atomergic Chemetals Corp., 100 Fairchild Avenue, Plainview, New York, N.Y. 11803 (USA).

(6) Sigri Elektrographit, Postfach 1160, D-8901 Meitingen (RFA) (quality "Sigradur"), Telex 05 3823 Sigri d, Tel. (08271) 83 3147.

*(7) Deutsche Carbon, D-6000 Frankfurt, Postfach 56 0209 (RFA).

(8) Metrohm Ltd, CH-9100 Herisau (Switzerland).

* Sellers only : (5), (7) : Le Carbone Lorraine.

APPENDIX B : TABLE OF ELECTROACTIVITY RANGE

Solvent : H_2O

Supporting Electrolyte (conc.)	Anodic limit - in Volt - (current density in $\mu A\ cm^{-2}$)	Cathodic limit - in Volt - (current density in $\mu A\ cm^{-2}$)	Reference Electrode	Temp. °C	Source n°
Na_2SO_4 (0.2 M) + Phosphate (0.05 M) 7 < pH < 9	+ 0.9 (80)	- 1.6 (80)	SCE		(3)
KNO_3 (0.5 M)		- 1.4	SCE	25	(4)
CH_3COOH (0.2 M) + $CH_3COO\,Na$ (0.2 M)	+ 1.5	- 1.0	Ag/AgCl, KCl sat	25	(4)
$HCOOH$ (0.2 M) + $HCOO\,Na$ (0.2 M)	+ 1.2	- 0.8	Ag/AgCl, KCl sat	25	(4)
NH_4NO_3 (0.05 M) + NH_3 (0.4 M)	+ 1.0	> - 1.0	Ag/AgCl, KCl sat	25	(4)
Phosphate buffer (0.2 M) pH = 6.5	+ 1.4	- 1.3	SCE		(6)
$Na\,OH$ (1 M)	0.0	- 1.7	SCE		(6)
Salts of seawater, - pH 2	0.0	- 1.0	Ag , AgCl		(8)
- pH 5	0.0	- 1.4	Ag , AgCl		(8)

Supporting Electrolyte (conc.)	Anodic limit - in Volt - (current density in $\mu A\ cm^{-2}$) (* μA)	Cathodic limit - in Volt - (current density in $\mu A\ cm^{-2}$) (* μA)	Reference Electrode	Temp. °C	Source n°
KOH (0.1 M)	+ 0.5	- 1.4	SHE		(14)
Acetate buffer pH = 4.7	+ 1.4	- 0.7	SHE		(14)
5.10^{-2} M (NH_4CH_3OO + CH_3COOH) buffer					
-after polishing on emery paper 400	+ 1.5 (56)	- 1.25 (56)	SCE		(15)
-after polishing with 0.5 μ paste	+ 1.6 (28)	- 1.4 (28)	SCE		(15)
H_2SO_4 (1 N)	+ 1.2 (45)	- 0.30 (45)	SCE	20	(17)
$NaClO_4$ (1 M)	+ 1.0 (1)*	+ 1.5 (1)*	SCE		(19)
CH_3COOH (0.1 M) + CH_3COONH_4 (0.2 M) pH = 5.0	+ 1.1 (7.9)	- 0.5 (7.9)	SCE		(20)
Phosphate and acetate buffers of pH=5 to 8, in CH_3OH and CH_3CN	∿ + 1	∿ - 0.8	Ag/AgCl, KCl (1M)		(22)
H_2SO_4 (1 M)	+ 1.5	- 1.0	SCE		(23)
H_2SO_4 (10 M)	+ 1.2 (25)	- 1.4 (25)	SCE		
HBr (1 M)	+ 0.7	- 1.5	SCE		(23)
None (electron photoemission)	+ 0.5	- 1.2	SCE		(25)
Na_2SO_4 (0.2 M)		- 1.2	SSCE		(30)
+ MeCN + Me_4NClO_4 (0.1 M)	> + 1.4	> - 1.6	SSCE		(30)
KCl ($5 . 10^{-2}$ M)	+ 1.1 (10)	- 0.8 (10)	SCE		(35)
HCl (1 M)	+ 0.7	- 1.0	SCE		(6)
HCl (0.01 M)	> + 0.075	< - 1.20	SCE		(21)
$HClO_4$ (0.1 M)	+ 1.2 (1)*	- 0.8 (1)*	SCE		(19)
$HClO_4$ (0.01 M)	> + 0.075	< - 1.20	SCE		(21)
$HClO_4$ (0.01 M) + NaSCN (0.1 M)	+ 0.45 (10)	- 2.3 (10)	SCE		(23)
NaSCN (2 M)	+ 0.35	- 2.5	SCE		

Supporting Electrolyte (conc.)	Anodic limit - in Volt - (current density in μA cm^{-2})	Cathodic limit - in Volt - (current density in μA cm^{-2})	Reference Electrode	Temp. °C	Source n°
$HClO_4 + KClO_4$ ($8 . 10^{-2}$ M) pH = 1.5	+ 1.7	- 1.0	SCE		(25)
$HClO_4 + KClO_4 + N_2O$ pH = ∿ 7	+ 1.7	- 1.5	SCE		(25)
$HClO_4$ (0.5 M) + O_2	0 (1)	- 0.4 (1)	NHE		(27)
Solvent : PC					
$LiClO_4$ (0.1 M)	+ 2.6 (1000)	- 3.2 (1000)	Fc/Fc^+		(16)
KPF_6 (0.1 M)	+ 3.6 (1000)	- 3.2 (1000)	Fc/Fc^+		(16)
Et_4NCl (0.1 M)	+ 0.4 (1000)	- 3 (1000)	Fc/Fc^+		(16)
Bu_4NPF_6 (0.1 M)	+ 3.6 (1000)		Fc/Fc^+		(16)
Solvent : Benzonitrile					
Bu_4NClO_4 (0.2 M)	+ 1.65	- 2.35	Fc/Fc^+		(16)
Solvent : Molten Salts					
$PbCl_2$ - KCl (77 - 23 % in mole)	+ 1.29 (1400)	0 (1400)	Pb/Pb^{II}	440	(9)
NaOH - H_2O (50 - 50 % in mole)	+ 0.1 (1400)	- 1.55 (1400)	Ag/Ag^I	100	(9)
Na_3AlF_6 (cryolithe)	+ 1.7	0	Al/Al^{III}	1015	(9)
$AlCl_3$ - NaCl	+ 2.15 (100)		Al, sat NaCl	175	(17)
LiCl - KCl	+ 0.25 (200)		Pt, Pt^{II} (0.1 M)	450	(17)
$CuCl_2$/KCl	+ 0.8 (< 10)	- 1.1 (< 10)	Ag/AgCl 0.02 % in solvent		(34)
$CO_3^=$ in LiCl-KCl eutectic, under P_{CO_2} = 1 atm	< + 0.2		Ag/Ag^+ (0.75 mol/kg)	470	(38)
$AlCl_3$-NaCl	+ 2.0	0	Al wire		(47)
$AlCl_3$-n-Butyl pyridinium chloride	+ 2.0	0	Al wire		(47)

Solvent : CH_3CN

Supporting Electrolyte (conc.)	Anodic limit - in Volt - (current density in $\mu A\ cm^{-2}$)	Cathodic limit - in Volt - (current density in $\mu A\ cm^{-2}$)	Reference Electrode	Temp. °C	Source n°
TEAP (0.1 M)	+ 1.1	- 2.25	$Ag, AgNO_3$ (0.01 M)	25	(4)
$LiClO_4$	+ 2.8	- 2.7	SCE + junction		(6)
TEAP (0.1 M)	+ 2.2		Ag/Ag^+ (0.01 M)		(12)
TEAP		- 2.1	SCE + junction		(18)
50 % C_2H_5OH + NaOH (pH ca.13.3)		- 1.75	SCE + junction		(18)
$C_4H_9NPF_6$ (0.5 M)		- 2.2 (5000)	Ag/Ag^+ (0.1 M)		(24)
Et_4NBF (0.10 M)	+ 3.5 (5000)				(26)
Solvent : THF					
$LiClO_4$ (0.3 M)		- 2.2			(12)
Solvent : n-CH_3 - $(CH_2)_2$ - CN					
$(n\text{-}Bu)_4NClO_4$ (0.10 M)		- 2.5	Ag/Ag^+ (0.01 M)	- 60	(26)
Solvent : DMF					
THAP (0.1 M)	+ 1.4 (325)	- 2.0 (325)	SCE	25	(28)
Solvent : 1,2 - $C_2H_4Cl_2$					
THAP (0.1 M)	+ 1.6 (325	- 1.9 (325)	SCE	25	(28)

APPENDIX C : TABLE OF VOLTAMMETRIC DATA

Table 1

Redox system or species (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details	Conc. of Red and or Ox in the solution (M)	Reaction observed oxidation reduction or both	Characteristic potential measured (V vs.Ref.el.)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	Ref. Electrode
(1) Ferrocene	CH_2Cl_2	0.1 M TBAP	CV	0 ↔ 900 mV 100 mV/s	10^{-3}	both	E_{pa} = + 0.677 E_{pc} = + 0.380	Quasi rev.		Ag/AgCl 1.0 M KCl
					10^{-4}	both	E_{pa} = + 0.554 E_{pc} = + 0.462			no corr.for junction potential.
(44) Ferrocene	H_2O (10 %) + C_2H_5OH (90 %)	0.2 M $NaClO_4$ + 0.01 M $HClO_4$	CV		$2 . 10^{-3}$	both		$(1.3 \pm 0.2)10^{-2}$		SCE
(28) Ferrocene	1,2-$C_2H_4Cl_2$	0.1 M THAP	HYV	0 → 1.6 V 100 mV/s	10^{-4}	oxidation	$E_{1/2}$ = + 0.52	Rev.	1	SCE (including junction potential.)
(1) $K_3Fe(CN)_6$	H_2O	1 M KCl	ACV	v = 10 mV/s 0 ↔ 400 mV ω = 10 - 100 Hz ampl = 10 mV P - P	(Ox) = $5 . 10^{-3}$	both	+ 0.238	$5.3 . 10^{-2}$	1	Ag/AgCl (KCl 1.0 mM no corr.for junction potential
(6) $K_3Fe(CN)_6$	H_2O	1 M KCl	CV 25°C	from v = 20 mV/s to 20 V/s	(Ox) = 10^{-3}	both	at 20 mV/s : E_{pc} = + 0.226 E_{pa} = + 0.285	$(7 \pm 1)\ 10^{-2}$		SCE
(7) $K_3Fe(CN)_6$	H_2O	0.5 M K_2SO_4	CV 25°C	1 to 3 V/s	(Ox) = $1.8 . 10^{-4}$	both	1/2(E_{pc} = + 0.265 + E_{pa})	$2.5 . 10^{-2}$	1	Ag/AgCl (KCl sat)

Redox system or species (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details	Conc. of Red and or Ox in the solution (M)	Reaction observed oxidation reduction or both	Characteristic potential measured (V vs.Ref.el.)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	Ref. Electrode
(10)										
$K_4Fe(CN)_6$	H_2O	0.5 M KCl	CV	from - 0.40 to + 0.75 V at 20 mV/s	(Red) = $1.0 \cdot 10^{-3}$	both	E_{p_a} = + 0.24 E_{p_c} = + 0.14	Quasi rev.	1	SCE
(14)										
$K_3Fe(CN)_6$ + $K_4Fe(CN)_6$	H_2O	0.1 M H_2SO_4	RDE V		$1 \cdot 10^{-3}$	both	$E_{1/2}$ = + 0.46	Rev.	1	SHE
"	H_2O	Phosphate buffer 1 M pH = 7	CV	100 mV/s	$1 \cdot 10^{-3}$ M	both		$\sim 10^{-4}$	1	
(39)										
$K_3Fe(CN)_6$	H_2O	0.1 M phosphate buffer + 1 M KCl pH = 3 7.4	CV	50 mV/s polished + heated (520 - 540°C)	$5 \cdot 10^{-4}$ $2 \cdot 10^{-4}$	reduction	$E_{p,c}$ = ($E_{p,a}$) + 0.235 (+ 0.292) + 0.231 (+ 0.281)		1	Ag/AgCl (4 M KCl)
(40)										
$K_3Fe(CN)_6$	H_2O	0.1 M phosphate buffer pH = 7.5	Turbulent tubular electrode (convective voltam.)	2.69 $ml.min^{-1}$ v = 0.2 $V.min^{-1}$	$1 \cdot 10^{-6}$ of each			(2 ± 1) 10^{-3}		Ag/AgCl (0.1 M KCl)
(44)										
$K_3Fe(CN)_6$ + $K_4Fe(CN)_6$	H_2O	0.5 M K_2SO_4	CV 22°C		$5.0 \cdot 10^{-3}$ of each	both		1.5 ± 0.2 10^{-2} on anodically "activated" GCE		SCE

Table 2

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak} other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(1) bis-hydroxy-methyl ferrocene	H_2O	KF - 0.1 M	CV	0 ↔ 900 mV 50 mV/s	10^{-3}	Both	$E_{p,a} = 0.280$ $E_{p,c} = 0.215$	Quasi-rev			
	H_2O	KNO_3 -0.1 M	CV	0 ↔ 900 mV 50 mV/s	10^{-3}	Both	$E_{p,a} = 0.277$ $E_{p,c} = 0.204$	Quasi-rev Quasi-rev			
	H_2O	KCl -0.1 M	CV	0 ↔ 900 mV 50 mV/s	10^{-3}	Both	$E_{p,a} = 0.268$ $E_{p,c} = 0.210$	Rev			
	CH_2Cl_2	TBAP -0.1 M	CV	0 ↔ 900 mV 50 mV/s	10^{-3}	Both	$E_{p,a} = 0.502$ $E_{p,c} = 0.422$	Quasi-rev			
	CH_3CN	TBAP -0.1 M	CV	0 ↔ 900 mV	10^{-3}	Both	$E_{p,a} = 0.424$ $E_{p,c} = 0.355$	Quasi-rev			
	CH_3CN	TEAPTS - 0.1 M	CV	0 ↔ 900 mV 50 mV/s	10^{-3}	Both	$E_{p,a} = 0.409$ $E_{p,c} = 0.330$	Quasi-rev		All potentials are vs. Ag/AgCl (1.0 m KCl); no correction for junction potential.	
	CH_3CN	$TBAPF_6$ - 0.1 M	CV	0 ↔ 900 mV 50 mV/s	10^{-3}	Both	$E_{p,a} = 0.401$ $E_{p,c} = 0.332$	Quasi-rev			
(2)							$(Ep)_a$ $(Ep)_c$				Reference : Ag/AgCl 0.1M NaCl
HEFc	CH_3CN	0.1 M $NaClO_4$	CV	0.1 -0.7V, 0.1V/s	$1 . 10^{-4}$	Both	0.41 0.35	Rev	/		
$BHEF_c$	CH_3CN	0.1 M $NaClO_4$	CV	0.1 -0.7V, 0.1V/s	$1 . 10^{-4}$	Both	0.41 0.35	Rev	/		"
AF_c	CH_3CN	0.1 M $NaClO_4$	CV	0.1 -0.7V, 0.1V/s	$1 . 10^{-4}$	Both	0.42 0.38	Rev	/		"
BAF_c	CH_3CN	0.1 M $NaClO_4$	CV	0.1 - 0.7V, 0.1V/s	$1 . 10^{-4}$	Both	0.42 0.38	Rev	/		"

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/Ref.) $E_{1/2}$, E_{peak} , other ...)		Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
							$(Ep)_a$	$(Ep)_c$				
(2)												
HEF_C	aqueous	0.1 M NH_2CH_2COOH + 0.1 M NaCl	CV	0.1 -0.7V, 0.1V/s	$1 . 10^{-4}$	Both	0.29	0.22	Rev	/		Reference: Ag/AgCl, 0.1 M NaCl
$BHEF_C$	aqueous					Both	0.32	0.25	Rev	/		
AF_C	aqueous					Both	0.27	0.20	Rev	/		
BAF_C	aqueous					/	/	/	/	/		

α-hydroxyferrocene---HEF_C 1,1'-bis α-hydroxyl ferrocene---$BHEF_C$

acetoferrocene --- AF_C 1,1'-bis - acetoferrocene ------ BAF_C

(3)											
NADH ↓ $NAD^+ + H^+ + 2e$	H_2O	0.2 M Na_2SO_4 0.05M phosphate $7 < pH < 9$	PY and N.P.P. at the RDE + CV on RDE	from 0.0V to 0.9V scan rate up to $50\ V\ s^{-1}$	from 10^{-6} to 10^{-3}	Ox	+ 0.4 to + 0.5 V/ SCE		Irrev	2	+ 0.15 V	Strong adsorption of NAD^+

NADH = 1,4 - Dihydronicotinamide adenine dinucleotide.

(4)											
Tl(I)/Tl	H_2O	KNO_3 (0.5M)	CV	0 V — - 1.5 V	ca. $5 . 10^{-3}$	Red	Ep = - 0.7			1		Reference: SCE
			CA		ca. $5 . 10^{-3}$	Red	- 1.0 V					

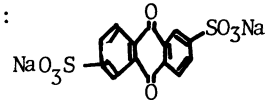
System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/red.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(4)											
$Ru(acac)_3$	CH_3CN	TEAP (0.1 M)	CV	1.1 V — - 2.0 V	10^{-3}	(III)/(II)	E_p				Reference:
						Red	- 1.12				$Ag/AgNO_3$
						Ox	- 1.12		1		0.01 M
						(III)/(VI)					
						Red	0.70		1		
						Ox	0.62				
			CA	- 1.4 V	10^{-3}	(III)/(II)					
						Red			1		
(Ru(H-edta) - (H_2O))	H_2O	CH_3COOH (0.2 M) + CH_3COONa (0.2 M)	HYV		10^{-3} - 5.10^{-3}	2 Ru(III)/ Ru (IV) - Ru (III)	$E_{1/2}$ 0.8		0.5		Reference: $Ag/AgCl$, KCl sat
						Ru (III)/ Ru (IV)	- 0.05		1		
						Ru (III)/ Ru (II)	- 0.3		1		
(6)											
SO_2	H_2O	1 M HCl	DPV	RDE 400 RPM Range - 0.3 V to - 0.6 V	10^{-5}	Red	E_p - 0.475 V	Irrev			Reference: SCE
$S_4O_6^=$	H_2O	0.2 M Phosphate buffer, pH = 6.5	DPV	RDE 400 RPM Range + 0.5 V to + 1.5 V	10^{-4}	Ox	E_p + 1.30 V	Irrev	2 e		"
$S_2O_3^=$	H_2O	0.2 M Phosphate buffer, pH = 6.5	DPV	RDE 400 RPM + 0.5 - + 1.5 V	10^{-5} - 10^{-3}	Ox	E_p + 0.95 V	Irrev	2 e		"

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(6) $(Ru(4,4'\text{-di-X-}2,2'\text{-dpy})_2NO_2NO)^{+2}$ X = substituent listed in Col.8	CH_3CN	0.5 M TBAP F_6	HYV	RDE 900 RPM Range +1.0 to -1.5 V vs Ag/Ag^+	10^{-2} - 10^{-4}	Red	$E_{1/2}$ X = Cl +0.005 H -0.043 C_6H_5 -0.082 C_4H_9 -0.116 CH_3 -0.140 OCH_3 -0.275	0.1 cm/sec	1e		
Dibenzothiophene	CH_3CN	0.2 M $NaClO_4$	CV	+1.00 V - 2.40 V SR 50 mV/sec	10^{-3}	Ox	E_p +1.25 V E_p +1.57 V E_p +1.95 V		1e 1e 1e		Reference: Ag/Ag^+ (0.1 M)
Dibenzothiophene	CH_3CN	0.2 M $NaClO_4$	HYV	RDE 400 RPM SR 2 mV/sec	10^{-3}	Ox	$E_{1/2}$ +1.18 V		1e		"
Benzothiophene	CH_3CN	0.1 M $LiClO_4$	CV	SR 100 mV/sec	10^{-3}	Ox	E_p +1.40 V		1e		"
Benzothiophene	CH_3CN	0.1 M $NaClO_4$	HYV	RDE 400 RPM SR 2 mV/sec	10^{-4}	Ox	$E_{1/2}$ 1.52 V		1e		"
Cyanocobalamin	H_2O	0.05 M acetate buffer, pH = 4.6	HYV	RDE 400 RPM SR 2 mV/sec	10^{-4}	Red	$E_{1/2}$ -0.80 V	Irrev	2e		Reference: SCE
Cyanocobalamin	H_2O	0.05 M acetate buffer, pH = 4.6	CV	SR 10 mV/sec Range +0.2 V to -1.2 V	10^{-4}	Red Ox Ox	E_p -0.93 V E_p -0.83 V E_p +0.13 V	Irrev Irrev Irrev	2e 1e 1e		" " "

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak} other ...)	Rate constant (cm s^{-1}) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(6) Cyanocobalamin	H_2O	0.05 M phosphate buffer, pH = 7.0	CV	SR 10 mV/sec Range + 0.2V to - 1.2V	10^{-4}	Red Ox Ox	E_p - 0.93 E_p - 0.83 E_p + 0.13	Irrev Irrev Irrev	2e 1e 1e		Reference : SCE
Cyanocobalamin	H_2O	0.05 M carbonate buffer, pH = 10.0	CV	SR 10 mV/sec Range + 0.2V to - 1.2V	10^{-4}	Red Ox Ox	E_p - 0.93 E_p - 0.83 E_p + 0.13	Irrev Irrev Irrev	2e 1e 1e		"
Aquocobalamin	H_2O	0.05 M acetate buffer, pH = 4.6	CV	SR 50 mV/sec	10^{-4}	Red Red Ox Ox	E_p - 0.10 E_p - 0.93 E_p - 0.83 E_p + 0.13	Irrev Irrev Irrev Irrev	1e 1e 1e 1e		"
Cyanocobalamin	H_2O	0.05 M phosphate buffer, pH = 7.0	ACV	SR 2 mV/sec 20 Hz, amplitude 20 mV	10^{-4}	Red Red	E_p - 0.01 E_p - 0.818	Irrev Quasi-rev	1e 1e		"
Cyanocobalamin	H_2O	0.05 M acetate buffer, pH = 4.6	ACV	SR 2 mV/sec 20 Hz, amplitude 10 mV	10^{-4}	Red Red	E_p - 0.1 E_p - 0.805	$6 . 10^{-4}$ $6 . 10^{-3}$	1e 1e		"
Cyanocobalamin	H_2O	0.05 M carbonate buffer, pH = 10.0	ACV	SR 2 mV/sec 20 Hz, amplitude 10 mV	10^{-4}	Red Red	E_p - 0.1 E_p - 0.89	$< 10^{-4}$ $4 . 10^{-3}$	1e 1e		"
Aquocobalamin	H_2O	0.05 M acetate buffer, pH = 4.6	ACV	SR 2 mV/sec 20 Hz, amplitude 10 mV	10^{-4}	Red	E_p - 0.06 E_p - 0.87	$5 . 10^{-3}$ $1 . 10^{-2}$	1e 1e		"
Hydroxyco-balamin	H_2O	0.05 M carbonate buffer, pH = 10.0	ACV	SR 2 mV/sec 20 Hz, amplitude 10 mV	10^{-4}	Red Red	E_p - 0.1 E_p - 0.89	$< 10^{-3}$ $6 . 10^{-3}$	1e 1e		"
Hemato-porphyrin	DMF	6 M H_2O	DPV	Range - 0.3 V to - 1.3 V vs SCE (NaCl) SR 1 mV/sec	10^{-3}	Red Red Red	E_p - 0.42 E_p - 0.55 E_p - 0.90	Quasi-rev Quasi-rev Quasi-rev	1e 1e 2e		Reference : SCE (NaCl)

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(6)											Reference :
Hemato-porphyrin	DMF	6M H_2O 1.5M $HClO_4$	CV	SR 10 mV/sec	10^{-3}	Red Red Red	E_p - 0.5 E_p - 0.7 E_p - 0.9	Quasi-rev Quasi-rev Quasi-rev	1e 1e 2e		SCE
$SbCl_6^-$	H_2O	12M HCl	HYV	Range + 0.7 V to 0.0 V, RDE 400 RPM	10^{-3}	Red	$E_{1/2}$ + 0.45	$2 . 10^{-3}$	2e		SCE
$SbCl_6^-$	H_2O	6M HCl	HYV	RDE 400 RPM	10^{-3}	Red	$E_{1/2}$ + 0.45	$2 . 10^{-3}$	2e		SCE
$SbCl_5OH^-$	H_2O	6M HCl	HYV	RDE 400 RPM	10^{-3}	Red	$E_{1/2}$ + 0.40	Irrev	2e		SCE
$SbCl_4(OH)_2^-$	H_2O	6M HCl	HYV	RDE 400 RPM	10^{-3}	Red	$E_{1/2}$ + 0.05	Irrev	2e		SCE
$SbCl_6^-$	H_2O	12M HCl	CV	SR 50 mV/sec	10^{-3}	Red Ox	E_p + 0.513 E_p + 0.607	$1 . 10^{-3}$	2e 2e		SCE
$SbCl_6^-$	H_2O	6M HCl	CV	SR 50 mV/sec	10^{-3}	Red Ox	E_p + 0.582 E_p + 0.678	$2 . 10^{-3}$	2e 2e		SCE
$SbCl_5(OH)^-$	H_2O	6M HCl	CV	SR 50 mV/sec	10^{-3}	Red	E_p + 0.350	Irrev	2e		SCE
$SbCl_4(OH)_2^-$	H_2O	6M HCl	CV	SR 50 mV/sec	10^{-3}	Red	E_p + 0.10	Irrev	2e		SCE
SO_2	H_2O	0.1M HCl 0.1M KCl pH = 1.0	HYV	Range 0.0 to - 0.08 V RD 400 RPM	10^{-3}	Red	$E_{1/2}$ - 0.48	Irrev	2e		SCE
SO_2	H_2O	0.1M HCl 0.1M KCl pH = 1.0	CV	SR 100 mV/sec	10^{-3}	Red Ox	E_p - 0.49 E_p - 0.02	Irrev	2e 2e		
SO_2	H_2O	0.1M HCl 0.1M KCl pH = 1.0	DPV	RDE 400 RPM	10^{-3}	Red	E_p - 0.51	Irrev	2e		

System studied (Rex/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant (cm s^{-1}) at standard redox potential	n F/mole	$E_{1/2}$ of E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(7)				Range of Scan Rates (V s^{-1})							
$Cr(III)/Cr(II)$	H_2O	1 M KCl	L SV	0.04 - 0.2	$Cr(III) = 2.06 . 10^{-3}$	Red	$E_{pa} = +1.000$ at 0.2 V s^{-1}	$1.27 . 10^{-4}$	1		Rapid poisning
$Ce(IV)/Ce(III)$	H_2O	1 M H_2SO_4	L SV	0.02 - 0.2	$Ce(IV) = 4.2 . 10^{-3}$	Red	$E_{pa} = 1.410$ $E_{pc} = 0.690$ at 0.2 V s^{-1}	$5.3 . 10^{-5}$			
IO_3^-/I^-	H_2O	1 M NaOH	L SV	0.02 - 0.12	$(IO_3^-) = 4 . 10^{-3}$	Red	$E_p = -1.319$ at 0.1 V s^{-1}	$2.1 . 10^{-19}$ at + 0.63 V	6		No chromic acid pre-treatment Ref.:Ag/AgCl, KCl sat
Fe^{3+}/Fe^{2+}	H_2O	0.5 M K_2Ox	CV, 25°C	0.04 - 0.20	$Fe(III) = 4 . 10^{-3}$	Both	$E_{p,av}$ = " +0.216	$1.4 . 10^{-3}$	1		Rate constant halved in 40 mn
	H_2O	0.9 M $HClO_4$	CV	0.04 - 0.20	$2 . 10^{-3}$	Both	" +0.533	$1.34 . 10^{-3}$	1		
	H_2O	0.45 M H_2SO_4	CV	0.006 - 0.2	$2 . 10^{-3}$	Both	" +0.467	$8.6 . 10^{-4}$	1		
	H_2O	0.09 M HCl	CV	0.02 - 0.2	$2 . 10^{-3}$	Both	" +0.520	$1.8 . 10^{-3}$	1		$E_{p,av} = 1/2(E_{pa} + E_{pc})$
		0.09 M + 0.1 M HCl ClO_4	CV	0.02 - 0.4	$2 . 10^{-3}$	Both	" +0.522	$5.7 . 10^{-3}$	1		
		0.09 M + 3.9 M HCl $NaClO_4$	CV	0.02 - 0.4	$2 . 10^{-3}$	Both	" +0.520	$1.2 . 10^{-3}$	1		
		1 M H_2SO_4	RDE V	Steady State	$2 . 10^{-3}$ Fe^{2+} / $2 . 10^{-3}$ Fe^{3+}	Both	NA	$9.0 . 10^{-4}$			
		1 M H_2SO_4	CV	NA	$2 . 10^{-3}$ Fe^{3+}	Both	NA	$1.2 . 10^{-3}$			

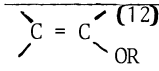
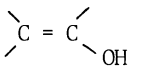
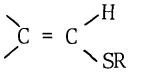
System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l (*in p.p.b.)	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(8) Trace metals											
Cd/Cd^{++}	H_2O	NaCl/HCl	Differential	from +1.0 V to 0 V	* From 5	First		Rev			
Pb/Pb^{++}	H_2O	≈	pulse	SR 10 mV/s	to	Red,					
Cu/Cu^{++}	H_2O	0.5 M	anodic		0.001 ppb	then					
Bi/Bi^{+++} Zn/Zn^{++}	H_2O	(Sea water)	stripping voltammetry			Ox					
(11) $W(CN)_8^{3-/4-}$	H_2O	0.2 M KCl	CV	SR 100 mV/s	$2.5\ 10^{-3}$ $K_4W(CN)_8$	Both	E_{pa} + 0.37 E_{pc} - 0.21		1		Reference : SCE
Several quinone / hydroquinones e.g. : 		0.2 M KCl	CV	SR 100 mV/s	Sat (Ox)		E_{p+} = -0.505 E_{p-} = - 0.59 (O_2-glow discharge treated GC)		2		Reversibility of the system increases drastically after exposing the polished GC surface to an O_2 glow-discharge.
(16) Ag/Ag^+	PC	Bu_4NPF_6	POT		10^{-3}_10^{-1}		E'^o = 0.50		1		Reference : Fc/Fc^+
$Ag(bipy)^+$ / $Ag(bipy)_2^{2+}$	PC	Bu_4NPF_6	POT,CV,RDE CA,EL		10^{-3}_10^{-1}	Oxid. of Ag(I) to Ag(II)	E'^o = 0.59	Rev	1		"
Co TPP	BN	Bu_4NPF_6	CV		10^{-3}	Co(III) → Co(II) → Co(I)	0.1 ; -1.3	Rev	1 ; 1		"

System studied (Rex/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(16)											Reference: Fc/Fc^+
Co_2FTF	BN	Bu_4NPF_6	CV, CA		10^{-3}	$(^{III}_{III}) \rightarrow (^{II}_{II}) \rightarrow (^{I}_{I})$	0.2 ; -1.3	Rev	2 ; 2		sep. of the two peaks for $(^{II}_{II}) \rightarrow (^{II}_{I}) \rightarrow (^{I}_{I})$
Co_2Clam	BN	Bu_4NPF_6	CV, CA		10^{-3}	idem	0.2 ; -1.3		2 ; 2		
Co_2 anticlam	BN	Bu_4NPF_6	CV, CA		10^{-3}	idem	0.2 ; -1.3	Rev	2 ; 2		
$Co_2$4C4	BN	Bu_4NPF_6	CV, CA		10^{-3}	idem	0.0 ; -1.7	Rev	2 ; 2		sep. of the 4 peaks : $(^{III}_{III}) \rightarrow (^{III}_{II}) \rightarrow (^{II}_{II}) \rightarrow (^{II}_{I}) \rightarrow (^{I}_{I})$
Co Pd 4C4	BN	Bu_4NPF_6	CV, CA		10^{-3}	$Co(III) \rightarrow Co(II) \rightarrow Co(I)$	0.1 ; -1.7	Q Rev	1 ; 1		
Co_2FTF_4	BN	Bu_4NPF_6	CV, RDE, CA EL		10^{-3}	$(^{III}_{III}) \rightarrow (^{III}_{II}) \rightarrow (^{II}_{II}) \rightarrow (^{II}_{I}) \rightarrow (^{I}_{I})$	0.15 ; -0.0 ; -1.4 ; -1.65	Rev	1 ; 1		
Co_2FTF_4	PC	Bu_4NPF_6	DPP , CV		10^{-3}	$(^{III}_{III}) \rightarrow (^{III}_{II}) \rightarrow (^{II}_{II})$	0.23 ; 0.1	Rev	1 ; 1		

System : - monoporphyrin : TPP = tetraphenylporphyrin

- biporphyrins : Co_2FTF , Co_2 clam , Co_2 anticlam , $Co_2$4C4 , Co Pd 4C4 , Co_2FTF_4

(see ref. 53, 54, 55 , Appendix D).

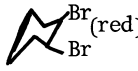
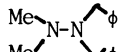
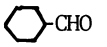
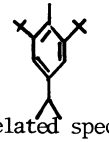
System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l (* in µg/l) (** P_{O_2})	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
 (12)	CH_2CN	TEAP 0.1 M	CV and macroelectrolyses	SR 0.1 V s^{-1}	3 10^{-3} for CV	Ox	$0.95 < E_p < 1.59$	Irrev	2		
	CH_2CN				$\simeq 10^{-2}$ for macroelectrolyses	Ox	$0.95 < E_p < 1.32$	Irrev	2		
	CH_2CN	Bu_4NBF_4	CV	SR 0.1 V s^{-1}	3 10^{-3}	Ox	$0.87 < E_p < 1.60$	Irrev	2		
(15) Ce^{3+}/Ce^{4+}		Acetate buffer 5.10^{-2} M	LSV	RDE 2 V/min 100 à 150 t/mn Pre-electrolysis at 1 V/ECS	8.10^{-5} à 8.10^{-5}	Red at -0.2 V/ECS			1 e^-		Reprod. 2,5 %
Cu Pb Cd	Sea water pH = 2		Anodic stripping Pulse Polarography.	-0.8 V → 0 V 3 mn pre-electrolysis DPP SR 2 mV s^{-1}	* < 1 µg/l		∿ as on Hg electrode				Hg film on GCE
(17) O_2/H_2O	H_2O	1 M HCl/KCl pH ≃ 3	CV	Prussian Blue (PB) modified GC	1 atm Ox **	O_2 Red.	$E_{1/2} \simeq +0.2$	Irrev O_2 Red is accelerated on PB film	4	$E_p = +0.2$ for ferro-ferricyanide	
Cl^-/Cl_2	Fused	LiCl - KCl (450°C)	CV								
Cr(III)/Cr(II)		LiCl - KCl (450°C)	CV					0.052 (450°C)			
ClO_2^+ / ClO_2		"	CV								

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experimen.details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole / l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(17)											
Fe(III)/Fe(II)		LiCl-KCl (450°C)	CV								
Cu(II)/Cu(I)		LiCl-KCl (450°C)	CV								
Cl^-/Cl_2	Fused	$NaCl-AlCl_3$ (175°C)	CV					$i_o = 8.6$ $\mu A/cm^2$ (175°C)			
(18)											
$SO_2/SO_2^{\cdot -}$	DMF AN	0.1 TEAP	CV El.	SR 10 - 500 mV/s	10^{-1}		E_p - 0.9V	Quasi	0.65		
(19)											
$Fe^{2+/3+}$	water	var.acids	HYV	+ 0.7 , - 0.1 V	0 - 6 . 10^{-3}	Red	$E_{1/2}$ + 0.44 → + 0.25	10^{-3} →> 10^{-2}	1	-	recalc to SHE
$Fe^{2/3+}$	water	var.compl. agents	HYV				+ 0.06 → - 0.325	10^{-3} → > 10^{-2}	1		recalc to SHE
Cu^0/Cu^{2+}	water	var.inorg. salts, HOAc, ethylene-diamine	HYV			Red	various	1 + 1 or 2			Reference : SCE

(For details see : J. Electroanal.Chem. 38, 349 (1972) ; 39, 229 (1972) ; 44, 117 (1973)).

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. Method used	Experim.details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant (cm s^{-1}) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(20) 3,4-Dihydroxybenzylamine	H_2O	0.1 M CH_3COOH	CV	+ 0.7 V - 0.0 V E_{init} = ± 0.0 V	10^{-4}	Both	E_{pa} = 0.49 E_{pc} = 0.20	Quasi-rev	2	E_{pa} = 0.275 E_{pc} = 0.125	Reference: SCE "
		0.2 M CH_3COOH_4 pH = 5.0		SR 5 - 200 mV s^{-1}			at SR 50 mV s^{-1}			at SR 50 mV s^{-1}	"
(23) Sb(V)/Sb(III)	9.5 M HCl		HYV	1.2 V ↔ - 1.0 V SR 10 mV . s^{-1} E_{init} = 0.6 V	10^{-3} - 10^{-2}	Red	$E_{1/2}$ = 0.47 (3000 rpm and 1 mM)	4 . 10^{-4}	2		Reference : SCE nα = 0.2 GC is stable in 9.5 M
Ce(IV)/Ce(III)	H_2SO_4	1 M	HYV	1.5 ↔ - 1.0 V E_{init} = 1.2	10^{-3} - 10^{-2}	Red	0.9 (3000 rpm) 10^{-2} M	3.2 . 10^{-4}	1		α = 0.25
Sn(IV)/Sn(II)	4 M HCl 9.5M LiBr	+ 1 M HBr	HYV	1.2 ↔ - 0.5 V	$10^{-3} \leftrightarrow 10^{-2}$	Ox	0.4 (3000 rpm) 7 mM	2 . 10^{-4}	2		nβ = 0.35
			HYV	0.0 ↔ - 0.7 V		Red	- 0.3	5.6 . 10^{-4}	2		nα = 0.32
Cu(II)/Cu(I)	KCl (+ HCl)	0.5 M (0.1 M)	HYV	1.2 ↔ - 1.0 V	10^{-3} - 10^{-2}	Both		(4.6 - 9.5) 10^{-3}	1		α=0.49-0.53
Ti(IV)/Ti(III)	H_2SO_4	1 - 10	HYV	1.2 ↔ - 0.8 V	10^{-3} - 4 10^{-3}	Ox	0.28 (3000 rpm) 1,5 mM		1		
Hg(II)/Hg(I)	H_2SO_4	1 M	HYV	1.5 ↔ - 1.0 V E_{init} = 1.0 V	10^{-5} - 10^{-2}	Red	0.43 (3000 rpm) 10^{-3} M	≪ 10^{-5}	≪ 10^{-5}		β = 0.32 - 0 α = 0.55
Hg(II)/Hg(I)	H_2SO_4	1 M	HYV	"	10^{-5} - 10^{-2}	Red	0.42	10^{-7}			nα = 0.55

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant (cm s^{-1}) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(24)											
I/II	CH_3CN	TBA PF_6 0.5 M	CV	+0.8 to - 2.2 Volt 0.02 V/s to 200 V/s 400 to 10 000 rpm	10^{-4} to 10^{-1}		$E_{1/2}$ + 0.005	0.06	1		Reference: Ag/Ag^+ (0.1 M)
III/IV	"	"	HYV	"	"	Red	$E_{1/2}$ - 0.043	0.19	1		
V/VI	"	"	"	"	"	Red	$E_{1/2}$ - 0.082	0.09	1		
VII/VIII	"	"	"	"	"	Red	$E_{1/2}$ - 0.116	0.07	1		
IX/X	"	"	"	"	"	Red	$E_{1/2}$ - 0.140	0.15	1		
XI/XII	"	"	"	"	"	Red	$E_{1/2}$ - 0.275	0.12	1		
Note : $(Ru(di\text{-}X\text{-}dpy)_2 (NO_2) (NO))^{1+/2+}$											
I/II , X = Cl V/VI , X = C_6H_5 (phenyl) IX/X , X = CH_3											
III/IV , X = H VII/VIII, X = C_4H_9 (But) XI/XII , X = OCH_3											
(25)											
Interactions C-Hydrogen C-H_2O C-Oxygen	H_2O	$HClO_4$ + $KClO_4$ 0.08 M	Electron photo - emission in electro-lytes + CV	Activation of the electrode	unknown in this method	Red very obvious. Perhaps Ox		very fast	1		
Reactivity of photogenerated atomic hydrogen $H \rightarrow H_3O^+$ $H \rightarrow H_2$				Study of the interactions							

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(26) 	n-PrCN	TBAP 0.10 M	LSV	From - 1.5 V to - 2.7 V SR 0.5 - 2 V/s - 60 to - 80°C	$1.5\ 10^{-3}$	Red of each conformer	E_p = - 2.0, - 2.3	Irrev	2		Reference : Ag/Ag^+ (0.01 M)
	CH_3CN	TEAP 0.10 M	CV	From - 0.2 V to + 0.5 V SR 0.02 - 0.1 V/s, 21°C	$\sim 10^{-3}$	Ox/Red	$E_{1/2}$ = + 0.20	$1.8 . 10^{-3}$	1		"
 $(CH_3)_3CCHO$	CH_3CN	TEAP 0.10 M	CV	From + 1.0 V to + 3.5 V SR 0.5 V/s	$2 . 10^{-2}$	Ox	E_p = + 3.0, + 2.9	Irrev	-		
 related species	CH_3CN	TEAP 0.10 M	CV	From + 2 V to - 2.2 V	10^{-3} - $5 . 10^{-3}$	Ox/Red	Many	-	-		Ref.: SCE
 others	57 % EtOH/ 43 % H_2O (Vol/Vol)	NaOH + $NaNO_3$ $(OH^-) = 10^{-2} \rightarrow 5$ M	CV	From ca. - 0.3 V to + 0.1 V SR 0.05 V/s, 25°C	$2 . 10^{-3}$	Ox/Red	$E_{p,c,a}$: - 0.04 → - 0.15 as a function of pH	Rev	1		Ref.: SCE

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim.details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(27)											
O_2/H_2O_2	H_2O	0.5M $KClO_4$	CV and HYV	From + 200 mV	C_{O_2} = $2 . 10^{-4}$	Red		Irrev		-	Reference: NHE
				to - 500 mV	$10^{-3} < C_{H_2O_2} < 10^{-2}$	$O_2 + 2e^- \rightarrow H_2O_2$	$E_{1/2} \simeq$ - 0.250			-	
H_2O_2	H_2O	0.5M $KClO_4$	CV and HYV	SR 1 to 100 $mV\ s^{-1}$		$H_2O_2 + 2e \rightarrow H_2O$	↓ positive catalysis by UPD of Pb. Shifts $E_{1/2}$ to $E_{1/2}$ = - 100 mV for O_2 reduction.			-	
(28)											
$CO_4(CO)_{12}$	1,2-$C_2H_4Cl_2$	THAP 0.1M	CV	0 → - 1.9 V and 0 → + 1.6 V SR 100 mV/s	$4 . 10^{-4}$	Both	E_{pc} = - 0.45	Rev	1	$E_{1/2}$ (Fc/Fc^+) = + 0.52 V/SCE	Reference: SCE
Pc H_2 (free base phtalocyanine)	1,2-$C_2H_4Cl_2$	THAP 0.1M	CV	0 → - 1.9 V and 0 → + 1.6 V SR 100 mV/s	$1.43 . 10^{-4}$	Both	E^1_{pc} = - 0.70	Rev	1		
							E^2_{pc} = - 1.1	Rev	1		
(30)											
$Ru(bpy)_3^{3/2+}$	H_2O	0.1M H_2SO_4	CV	E_{init} = 0.00 V 0.05 V/sec	10^{-3}	Ox	$E_{1/2}$ = 1.03	0.065	1		Reference: SSCE
$Ru(bpy)_3^{3/2+}$	H_2O	0.2M Na_2SO_4	CV	E_{init} = 0.00 V 0.05 V/sec	10^{-3}	Ox	= 1.01	Rev	1		

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(30)											
$Ru(bpy)_3^{3/2+}$	H_2O/CH_3CN 50/50	0.1 M TMAP	CV	E_{init} = 0.00 V SR 0.05 V/s	10^{-3}	Ox	$E_{1/2}$ = 1.15	Rev	1		Reference: SSCE
$Os(bpy)_3^{3/2+}$	H_2O	0.2 M Na_2SO_4	CV	"	10^{-3}	Ox	= 0.60	Rev	1		
$Cp_2Fe\,TMA^{2/+}$	H_2O	0.2 M Na_2SO_4	CV	"	10^{-3}	Ox	= 0.38	Rev	1		
bpy = 2,2' bipyridine.											
$Cp_2Fe\,TMA^+$ = (Tetramethylammonio)ferrocene.											
No correction for junction potential.											
(33)											
Hg/Hg_2^{2+}	H_2O	KNO_3	Potentio-static	From + 500 mV to - 500 mV	(M^{2+}) = 10^{-4} to 10^{-1}	Red and Ox		Rev	2		
Ag/Ag^+	(Deoxygenated with N_2)	(1 M)	Galvano-static	vs. the Rev potential of the respective M/M^{2+} electrode				in all cases	1		
Pb/Pb^{2+}									2		
Cu/Cu^{2+}									2		
(35)											
Fe^{2+}/Fe^{3+}	H_2O	0.1 M $HClO_4$	DCP (flow through	E_{init} = + 0 V/SCE	10^{-4}	Ox	$E_{1/2,a}$ = + 0.7	Irrev	1		Reference: SCE
						Red	$E_{1/2,c}$ = + 0.35	Irrev	1		"
		0.1 M $HClO_4$ + 10^{-3} M KCl		E_{init} = + 0.9 V/SCE	10^{-4}	Ox	$E_{1/2,a}$ = + 0.58	Irrev	1		"
						Red	$E_{1/2,c}$ = + 0.42	Irrev	1		"

System studied (Rex/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant (cm s^{-1}) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(5)	Me_2SO	TEAP	CV	I_{pc} / I_{pa}		Red of dissolved species	E_{pc} (± 0.01)				Reference : SCE E_{pc} if coupled to glassy carbon
C(T-(m-NH_2)PP)			CV	1			- 0.08 - 1.45				- 1.08 - 1.50
C(Fe^{III}T(p-NH_2)PP)			CV	1			- 0.11 - 0.17 - 1.68				- 0.13 - 1.17 - 1.65
C(Co^{III}T(m-NH_2)PP)			CV	1			+ 0.06 - 0.85				+ 0.10 - 0.86
C(Cu^{II}T(p-NH_2)PP)							- 1.20 - 1.68				- 1.19 - 1.65
C(Zn^{II}T(p-NH_2)PP)							- 1.31 - 1.72				- 1.39 - 1.75
C(Ni^{II}T(p-NH_2)PP)							- 1.18 - 1.75				- 1.21 - 1.78
(14)											
O_2	H_2O	0.1 M KOH	HYV	prepol. at + 0.25 and at - 1.25 V (1 min)	$3 . 10^{-4}$	Red	- 1.143	ca 10^{-4}	2		Reference : SHE
O_2	H_2O	0.1 M KOH	HYV	Anodic prepol. 20 µA for 2 min.	$3 . 10^{-4}$	Red	- 0.022	"	"		Reference : SHE

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l (* p.p.b.)	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(21) $Pb^{2+}/Pb(Hg)$	H_2O	0.01 M HCl or $HClO_4$	DCP - ASV	$E_{deposit}$ = -1.000 V E_{final} = +0.075 V E_{pulse} = 50 mV (60 ms) SR 1 to 5 mV. s^{-1}	Conc. in solut.* 0.025 to 100 ppb	Red Ox	E_{peak} = - 0.430 to - 0.530				Reference : SSCE
(28) Pb^{2+}/PbO_2	H_2O	CH_3COOH 1 M + $(CH_3COO)_2$ Pb 0.1 M	Potential step	Step from : 0 to + 275 mV at 40 to 60°C	(Pb^{II}) = 0.1	Ox					
(36) Ag^+/Ag	H_2O	$HClO_4$ 1.0 M	LSV	From + 0.80 to + 0.40 V	10^{-2}	Red	Electro-reduction starts ∿ + 0.650	Quasi-rev			Reference : NHE
(37) $NADH/NAD^+ + 2e + H^+$	H_2O	0.5 M KCl or 0.25 M K_2SO_4 + 0.05 M tris or Phosphate buffer (pH > 7)	RDE V	10 rps SR 2 mV s^{-1}	(Red) = 10^{-3}	Ox	$E_{1/2}$ = + 0.450 (± 0.01) V			Possibility ECE mechanism	Reference : SCE Electrode covered with adsorb. NAD^+
	H_2O		LSV	SR 5 mV s^{-1}	(Red) = 10^{-3}	Ox	E_p = + 0.475				

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(39)											
Ascorbate (Ascorbic acid)	H_2O	pH 7.4 (0.1M buffer) Ionic strengh to 1 with KCl	CV	SR 50 mV . s^{-1}	$5 . 10^{-4}$	Ox	E_p = + 0.390 V				Reference : Ag/AgCl. KCl 4 M Syst. more reversible on GC heated before use at 520°C/1 torr.
		pH = 3.0	CV	SR 50 mV . s^{-1}	$5 . 10^{-4}$	Ox	0.480				E_p: + 0.35 + 0.253
4 Me Cat (Methyl-catechol)	H_2O	pH = 3.0	CV	SR 50 mV . s^{-1}	$5 . 10^{-4}$	Ox	0.415	Irrev			+ 0.428
		7.4	CV	SR 50 mV . s^{-1}	$5 . 10^{-4}$	Ox	0.140				+ 0.132
DoPAC (3,4-dihydroxy-phenyl ethyl-amine-HCl)		pH = 3.0	CV	SR 50 mV . s^{-1}	$5 . 10^{-4}$	Ox	+ 0.590	Irrev			+ 0.437
		7.4	CV	SR 50 mV . s^{-1}	$5 . 10^{-4}$	Ox	+ 0.430				+ 0.155
DHBA (3,4-dihydroxy-benzylamine-HBr)		pH = 3.0					+ 0.710	∿ Rev			+ 0.460
							+ 0.360				+ 0.217
(46)											
2-Ethyl-anthraquinone	CH_3OH C_2H_5OH Propan-2-ol	Buffer : (0.1M NH_4Cl + 0.1M NH_3)	LSV and CV between 0 and - 1.0 V 20°C		∿ 10^{-3}		E_{p_c} = - 0.68 ± 0.01 V				Reference : SCE

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details (potential range explored, initial potential, scan rate, etc ...)	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant ($cm\ s^{-1}$) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ferricinium	REMARKS
(51)											
	H_2O	Britton-Rob. buffer (pH = 11.9) + Na_2SO_4 0.1 M	CV	SR 37 $mV.s^{-1}$	2.10^{-3}	Ox	E_{pa} (V)				Reference: SCE
Me_2NH							+ 1.03				
Et_2NH							+ 1.00				
Pr^n_2NH							+ 0.90				
Me_3N							+ 0.76				
Me_2NEt							+ 0.74				
Me_2NPr^n							+ 0.75				
Me_2NPr^i							+ 0.72				
Me_2NBu^t							+ 0.70				
$Me_2NCH_2CO_2^-$							+ 0.73				
$Me_2NCH_2CH_2CN$							+ 0.96				
$Me_2NCH_2CONH_2$							+ 0.93				
$Me_2NCH_2CH_2OH$							+ 0.76				
Me_2NCH_2Ph							+ 0.74				
$Me_2NCH_2CH_2NH_2$							+ 0.77				
Et_3N							+ 0.69				
Pr^n_2NMe							+ 0.65				

System studied (Red/Ox) (Source n°)	Solvent	Supporting electrolyte (conc.)	Electrochem. method used	Experim. details (potential range explored, initial potential, scan rate, etc ...	Conc. of Red and/or Ox in the solution in Mole/l	Reaction observed Oxidation Reduction or Both	Characteristic Potential measured (V/ref.) ($E_{1/2}$, E_{peak}, other ...)	Rate constant (cm s^{-1}) at standard redox potential	n F/mole	$E_{1/2}$ or E_{peak} of ferro-ferricyanide or ferrocene/ ferricinium	REMARKS
(52)	H_2O	Phosphate buffer (pH = 12) 0.1 M Na_2HPO_4 - NaOH, 0.1 M Na_2SO_4	CV		$5 . 10^{-3}$ to $2 . 10^{-2}$		1/2 (E_{pc}+E_{pa}) (V)				Reference : SCE
Me_2NEt							+ 0.67				
Me_2NPr^n							+ 0.66				
Me_2NPr^i							+ 0.63				
Me_2NBu^t							+ 0.62				
$Me_2N-CH_2CH_2OH$							+ 0.67				
Me_2N-CH_2Ph							+ 0.64				
$Me_2N-CH_2CO_2H$							+ 0.63				

APPENDIX D : SOURCE LIST

a) Answers to the questionnaire

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Errata

Volume, Issue and Year	Page no. and location	Correction
56, 8 (1984)	1102 Solvent: Molten Salts Column 1, item 6	for $CuCl_2/KCl$ read $CaCl_2/KCl$
57, 6 (1985)	903 Section 6.4 line 1	for cholesterol oxygen oxidoreductase read cholesterol oxidase suspension
	903 Section 6.5 line 1	for (catalase-suspension 1) read (catalase-suspension)
	903 Section 7.2 line 3	for catalase-suspension 1 (6.5) read cholesterol oxidase suspension (6.4)