

METHODS OF CHEMICAL ANALYSIS

COULOMETRIC ANALYSIS. DIRECT COULOMETRY (REVIEW)

T. K. Khamrakulov and V. V. Chervyakova

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Papers on the determination of inorganic materials by the direct coulometry (DC) method published in 1966-1974 are considered in the review.

In DC the content of material is established from the amount of electricity consumed for direct electrotransformation of the electroactive component. The determination can be carried out with a controlled potential ($E = \text{const}$) or controlled amount of current ($i = \text{const}$) as a function of conditions.

Despite the relative complexity of the experimental technique and the apparatus used DC attracts the attention of investigators because of the selectivity of the method and high accuracy and reproducibility of results of quantitative determination. A series of new variations of DC has appeared recently and the number of investigations on the theory of coulometry, equipment, coulometers, electrolyzers, and electrodes has increased. Papers are devoted mainly to the increase in precision, accuracy, and speed of analytical results (taken together or separately) with the simultaneous removal of the necessity of using complex equipment. For example, these are coulopotentiography [1], coulopotentiography with anodic solution of the precipitate [2], coulostatic method [3], chronocoulometry [4], substoichiometric coulometry [199], and variations of current integrators [5-7].

Certain aspects of theory and potentialities of DC for the determination of uranium, transuranium elements, gases, and liquids are examined in [8-10].

The analytical use of DC at $E = \text{const}$ and $i = \text{const}$ for analysis of inorganic materials and their compounds is illustrated by Tables 1 and 2. It is seen from data of the tables that DC is applicable to the determination in nonaqueous solutions of the following elements: s^1 : H₂, Li, Na, K; s^2 : Be, Mg, Sr, Ba; p^1 : In, Tl; p^2 : C, Sn, Pb; p^3 : N₂, As, Sb, Bi; p^4 : F, Cl, Br, I; d^2 : Ti; d^3 : V; d^4 : Nb, W; d^5 : Cr, Mo, Mn, Tc, Re; d^6 : Fe; d^7 : Co, Ru, Ir; d^8 : Ni, Rh, Pt; d^9 : Pt; d^{10} : Pd, Cu, Ag, Au, Zn, Cd, Hg; f^2 : Ce; f^3 : U; f^4 : Pm; f^6 : Sm; f^7 : Eu, Am; f^{14} : Yb.

DC is used most widely for the determination of p- and d-elements and for uranium and plutonium of f-elements.

Fuel and inert gases [11-16], solutions of acids and bleaching vats [27-29], products of chemical reactions and chromatographic analysis [42, 43], steels, alloys [117, 118], standard solutions [120, 131], and industrial and natural objects [123-128, 137-139, 143, 144] are analytical objects. Apart from the most frequently used electrodes (Pt, Hg, Au) glassy graphite [131, 132, 156, 159], carbon pyroceramic [161], and the rotating disc electrode [134] are proposed for the working electrode.

The potentialities of DC are restricted significantly during the determination of the elements: s^1 : Li, Na, K, Rb, Cs; s^2 : Be, Mg, Ca, Sr; p^1 : Al, Ga; d^1 : Sc, Y, La, Lu, Ac; d^2 : Zr, Hf; d^3 : Ta, and also of certain lanthanides and actinides. These difficulties are due mainly to the electronic configuration of the indicated elements, their negative standard electrode potentials (E^0), and ability to be oxidized easily and to form stable compounds, from which they are subsequently electroreduced with difficulty. Naturally E^0 is not an absolute characteristic of the oxidation-reduction ability of systems, since the course and rate of the electrochemical process can be changed as a function of various factors, for example, nature of solvent. Therefore, it can be asserted that the use of DC for the determination of elements indicated above is a concern of the near future and success is evidently guaranteed upon using

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TABLE 1. Direct Coulometry ($E = \text{const}$). Accepted abbreviations: W is the working electrode, A is the auxiliary electrode. I) Potential is transmitted to the working electrode from an external current source, a potentiostat; II) potential is transmitted to the working electrode from a chemical current of a galvanic element.

Determined component	Analyzed object	Determinable amounts	Potential of the working electrode, rel. s.c.e.	Experimental conditions, Interfering ions	Literature
1	2	3	4	5	6
H_2	Fuel gases	Microquantities	-0.04	W is Pt or Pd, coated with platinum black, I	6
	Helium, nitrogen, saturated hydrocarbons	$10^{-4} - 10^{-3}\%$	0.1-1.0	$H_2 \rightarrow HCl$, $H_2 \rightarrow H_2O$, 6M KOH, W is pyrographite coated with Pt black, A is metalloceramic porous Pd, II	11
	Solutions		0.6-0.8	$H_2 \rightarrow H_2O \rightarrow O_2$, 5 M KOH, W is Ni, A is Ni, II	12-16
H^+					17
H_2O	Gases, organic compounds	10^{-8} mole/liter	0.2-0.4	Analyzed solution, A is Ag/AgCl, W is Pt, II	18
	Natural objects, hydrocarbons, inert gases	2 mg/m ³	-	Polymeric film, adsorbing H_2O , W is Pt, A is Pt, I, II	19, 20
	Water, adsorbed on ThO_2	0-10 ppm 60	-	$H_2O \rightarrow H_3PO_4$, P_2O_5 , deposited on a Pt electrode, W is Pt, A is Pt, II	15, 21-26
Acids and Bases				P_2O_5 deposited on a Pt electrode, W is Pt, A is Pt, II	27
H_2O_2	Solutions of acids and bases	Microquantities			28-29
	Solutions of bleaching vats	Microquantities	0.7-0.9	H_2O_2 , O_2 , 25% NaOH solution, W is porous Ag, II	30
Li (I)	Solutions	2 mg-eq	-	Acetonitrile + tetraethylammonium perchlorate, W is Hg, I	31, 32
CO	Gas mixtures	1-100 ppm	0.65-1.25	$CO \rightarrow CO_2$, W is polyfluoroethylene resin Pt gas-diffusion, I	33
	Gases, molten metal	Microquantities	0.2-0.4	Solid I_2O_5 , $t = 140^\circ C$, $CO \rightarrow I_2$, $CaCl_2 + 5\%$ CaC_2 , W is Pt, A is Hg, C, II	34-35
C, CO_2	Molten metal, generator gas	Microquantities	-	$CaCl_2 + 5\%$ CaC_2 , W is metal, A is $CO + CO_2$ mixture, II	232
CO_2	Gases, atmospheric air	Microquantities	0.2	KOH solution, W is Pt, Pd, PdH_2 ; A is Hg, Ag/AgCl, II	16, 36-38
$C_2O_4^{2-}$	Solutions	$10^{-9} - 10^{-6}$ N	1.6	0.5 M H_2SO_4 , W is graphite filament, I, Cr(VI), Cl(IV), Fe(II), U(VI) interfere	39

NO ₂ ⁻	Gases	4 mg	0.95	1 M in CH ₃ CO ₂ H and CH ₃ CO ₂ Na, pH 4.7, I. SCN ⁻ , Mn(II), Sb(III) interfere	40
NO, HNO ₂	Chemical reaction products	10 ⁻⁶ —10 ⁻³ M	(-0.09)+(-1.25)	0.5 N Na ₂ HPO ₄ , pH 5-7, 0.5 N in Na ₂ SO ₄ and NaH ₂ PO ₄ , W is Hg, I	41
NO	N ₂	10 ⁻⁷ —10 ⁻⁸ %	-0.3	NO→NO ₂ . Quartz saturated with FeSO ₄ , t = 350°C, KMnO ₄ in 10% H ₂ SO ₄ , 0.01 KI, W is Pt, A is Pt, I	241
NO, NO ₂	Gas mixtures	Trace amounts	0.2—0.4	NO→NO ₂ . Glass wool saturated with electrolyte solution. W is Pt, A is activated carbon, silver II. Products of acidic and basic character interfere	42
	Products of chromatographic analysis	10 ⁻⁶ —10 ⁻⁴ %	0.3	NO→NO ₂ , 0.01 M KI, W is Pt, A is Ag, C, II	43
	Air, exhaust gases of internal combustion engines	0.02 mg/liter	0.2—0.4	NO→NO ₂ , 1% solution in H ₂ SO ₄ and 3% in KBr, W is Pt, A is activated carbon, Ag, II, H ₂ S, SO ₂ , SO ₃ , NH ₃ , hydrocarbons interfere	44—46
NH ₃	Products of chromatographic analysis, gases	10 ⁻⁶ —10 ⁻⁴ %	0.2—0.4	NH ₃ →NO ₂ , 0.1 M KI, W is Pt, NH ₃ →NH ₄ ⁺ , 2 M Na ₂ SO ₄ , W is Al, A is C, II	43, 47
O ₂	Inert and fuel gases	Microquantities	(-0.6)—(0.8)	5 M KOH, W is Ni or Pt, coated with platinum black, A is Ni, II	48—11, 17
	Sewage	3 µg/liter	(-0.5)—(-0.6)	0.1 M HCl + 0.05 M Na ₂ B ₄ O ₇ , W is Pd, A is Ag/AgCl, II	49—52
O ₃	Magnesiowüstite	Milligram quantities	0.35—0.55	1 N H ₂ SO ₄ , W is magnesiowüstite, I	53
	Aqueous solutions, SAM, organic materials	1 µg/liter	-0.6	KOH solution, 2 M NaClO ₄ + 2 M NaI, W is Pb, Au, or Ag, A is Ag, II	54—60, 239
	Gases, steels	Microgram	-0.6	Zr ₂ —MgO and ThO ₂ —V ₂ O (solid electrolyte), W is metal, A is metal oxide, II	61—63
	Electrolyte solutions	Microgram quantities	(-0.5)—(-0.7)	CH ₃ CO ₂ H solution, W is Ag, Au, A is Ag, Pb, II. Diffusion barrier of polyfluoroethylene resin or polyethylene. CO, H ₂ S, C ₂ H ₂ , H ₂ SO ₄ , NO interfere	64, 65
	Gases, dissolved oxygen	Microgram quantities	(-0.5)—(-0.7)	Ca and Zr salts (solid electrolyte), KOH solution, W is porous metal, Ag, A is CD, stainless steel, II	65—86
	Peroxides, hydroperoxides	Microgram quantities	(-0.6)—(-0.8)	KOH solution, W is Au, A is Pb, Zn, II	87
	Sulfuric acid solutions	Microgram quantities	(-0.5)—(-0.7)	Acetate buffer, W is Au, A is Pb, II	88

Table 1. (Continued)

Determined component	Analyzed object	Determinable amounts	Potential of the working electrode, rel. s.c.e.	Experimental conditions. Interfering ions	Literature
1	2	3	4	5	6
	Alcohols, SAM, gas mixtures, solutions	0.2%	-0.6	27% KOH, diffusion barrier of polyethylene, W is Ag, A is a pressed cadmium shaving or Cd, II	89-91
	Gases, electrolyte solutions	0.2 µg	(-0.6)-(-0.8)	KOH solution, W is Ag, A is Pb, foil, II	73, 90
	Steels	3·10 ⁻⁴ -1%	1.0	25% KOH, W is Pt, A is Ag, II	92
	Organic materials in water, air	Microquantities	(-0.6)-(-0.8)	Oxidation of contaminating materials with CrO ₃ or MnO ₂ , H ₂ O ₂ solution, W is Ag, A is Zn or Cd, II	93
O ₂	Air	0.05-1 µg/m ³	0.2-0.5	2% NaBr + 0.1% NaH ₂ PO ₄ + 0.01% NaI + Na ₂ HPO ₄ , W is Pt, A is carbon, II. Materials reacting with ions interfere	94, 95
O ₂	Air	0.04 µg/m ³	0.2-0.5	KBr or KI solution, W is Pt, A is C, Pb, or Ag	96-98
F ₂	Atmosphere	Microquantities	0.5-0.7	LiCl→CdI ₂ solution, W is Pt, A is Ag/AgCl, II	99, 100
Na ⁺	Sodium Salts	2mg-eq	-2.45; -0.50	Na ⁺ →Na→Na ⁺ , acetonitrile + tetraethylammonium perchlorate, W is Hg, II	31, 32
Mg (II)	Eluate				101
S	Sulfur compounds	5-20 mg	0.85; 0.50; 0.80	1 N HCl, phosphate buffer, Clark and Lubs buffer solution, W, A are Pt, I	102
$\begin{matrix} \text{S}_2\text{O}_3^{2-} \\ \text{S}^{2-}, \text{SCN}^- \end{matrix}$	Aqueous solutions	Microgram		HClO ₄ solution, Na ₂ SO ₃ , CH ₃ CO ₂ H, CH ₃ CO ₂ Na, I. W is amalgamated Ag	103-105
SO ₂ , H ₂ S, CS ₂	Atmosphere	Microgram	0.2-0.5	KI solution, W is Pt, A is carbon+MnO ₂ , II	51, 106-108
		0.1-0.3 ppm 60	The same	Iodine solution, W is Pt, A is carbon+MnO ₂ , II, HCN interferes.	109, 110
Cl ₂	Air	Microquantities	0.1-0.2	25% LiCl + 0.02% LiBr + 4% acetamide; 3M NaBr + 1·10 ⁻³ M NaI, 0.1 M Na ₂ HPO ₄ + 0.1 M NaH ₂ PO ₄ , 10% HCl, W is Ag, Pt, Au, A is porous silver, Ag/AgCl, II. SO ₂ , NO ₂ interfere;	111, 114
HCl chlorinated hydrocarbons	Air	Microquantities	0.4-0.7	HCl→Cl ₂ , Hydrocarbons→HCl→Cl ₂ , 25% LiCl + 0.02% LiBr + 4% acetamide, W is Pt, A is porous silver, II	111
ClO ⁻	Industrial solutions of bleaching vats	Microquantities	-0.75	ClO ⁻ →O ₂ , 0.25% NaOH+KIO ₄ , W is porous silver, I	30
K ⁺	Potassium salts	Microquantities	(-2.0)-(-0.5)	K ⁺ →K→K ⁺ , 0.1 M KOH, W is Hg, I	32

Ca (II)				W is Hg, I		115
	Eluate, model solutions		0.05	Diethylenetriaminepentaacetic acid, pH 10, W is amalgamated Pt,		101-116
Ti (IV)			-0.20	9 M H ₂ SO ₄ , W is Hg, I. Se(VI), As(V), Bi(III), Te(VI), Cu(II), Mo(VI) interfere		117
			1.20 or 0.50	1.5 M H ₃ PO ₄ or 1.5 M H ₃ PO ₄ +0.05 M Na ₄ P ₂ O ₇		118
V (IV), V (V)			1.15	V(IV)→V(V), 1.5 M H ₃ PO ₄ , W is Pt		119
	V(IV) salt solutions			K ₂ Cr ₂ O ₇ +H ₂ O ₂ →O ₂ , W is Au, Ag, A is Zn, Cd, II. Reducing and oxidizing agents Cl ⁻ , Fe ³⁺ interfere		120
Cr ₂ O ₇ ²⁻	Standard K ₂ Cr ₂ O ₇ solutions	6·10 ⁻³ —4·10 ⁻² %	(-0.6)—(-0.8)	0.25 M Na ₄ P ₂ O ₇ , pH 2, W is Pt, I. Ti(II), As(V), V(III), Ce(III), Sb(III) interfere		121
Mn (II)	Solutions	0.5—10 mg in 25 ml	1.05—1.10	K MnO ₄ +H ₂ O ₂ →O ₂ , W is Ag, Au, A is Zn, Cd. Oxidizing and reducing agents, Cl ⁻ , Fe ³⁺ interfere		120
MnO ₄ ⁻	Standard KMnO ₄ solutions	0.2—1.8	(-0.6)—(-0.8)			
Fe (CN) ₆ ⁴⁻ , Fe (CN) ₆ ³⁻	Salt solutions	10—150 mg	0.54—0.84	0.5 M KCl, W is Pt, Ag, I. I ⁻ , SHN ⁻ interfere		105
Fe (II), Fe (III)	Wüstite	23—24%	0.2	0.05 M H ₂ SO ₄ , W is wüstite, I		123, 124
Fe (II)	Model solutions, standard samples	0.05—112 µg	0.12—0.48	1 M HCl, 1 M HClO ₄ , W is Au, Pt, I		125—127
	Oxide layers on iron samples	Microquantities	0.0	0.15 M in H ₃ BO ₃ and NaBO ₃ , pH 8.4, W is Fe sample, I		128
Fe	U-Al alloys, model solutions, nuclear fuel	1.92 mg	-0.05	W is Hg, I		129, 120
Fe (III)	Standard solutions	1 mg	0.56	1 M H ₂ SO ₄ , W is glassy graphite, I		131
Ni (II)	Eluate solution	Microquantities	-0.44	0.5 M H ₂ SO ₄ , W is glassy graphite, I		132
Cu (I)	CuBr solutions	Microquantities	-0.11	0.1 M in NaBr and NaNO ₃ , W is Cu, I		133, 31
		0.4 mg-eq	-0.50	0.25 M K ₂ SO ₄ , W is a rotating copper disc, I		134
	Standard Solutions	Microquantities	0.05	Diethylenetriaminepentaacetic acid, pH 5 or 10, W is amalgamated platinum, I		116
Cu (II)		2 mg-eq	-0.60	Cu(II)→Cu(I), acetonitrile + tetraethylammonium perchlorate, W is Hg, I		31
	Eluate	1·10 ⁻³ M	0.39	0.5 M HCl, W is glassy carbon, I		132

Table 1. (Continued)

Determined component	Analyzed object	Determinable amounts		Potential of the working electrode, rel. s.c.e.	Experimental conditions. Interfering ions		Literature
		3	4		5	6	
Zn (II)	Model solutions	Microquantities	-0.05	Diethylenetriaminepentaacetic acid, pH10, W is amalgamated platinum, I		106	
Se (IV)	Model solutions	Microgram quantities	-0.45	0.2-2.0 M HCl, 0.5 M citric acid, R is Au, Hg, I		135, 136	
Sr (II)	Strontium salts, eluate	10 ⁻⁴ g-eq	-1.5; -0.5	Sr(II)→Sr→Sr(OH) ₂ , W is Hg, I		32, 101, 115	
Mo (VI)	Mo-Re-W alloys	0.2-10 mg/liter	-0.25	0.2 M (NH ₄) ₂ C ₂ O ₄ + 1.3 M H ₂ SO ₄ , pH 2.1, W is Hg, I. Fe(III), Cu(II), Bi(III), Ti(IV) (removed with preelectrolysis) interfere		137	
Ru (IV)	Model solutions	0.2-2.0 mg/ml	0.5	6 M HCl, W is Pt, I. Ir(IV) interferes		138	
	Ru, alloys based on Ru	100 mg	0.05	5 M HCl, W is Hg, I		139	
Rh (III)	Concentrates after removal of noble metals	Milligram quantities	-0.2	0.2 M HCl, W is Hg, I		141	
Ru (X)	Model solutions	0.05 mg	-0.10; 0.80	Ru(X)→Ru(III)→Ru(IV). 1 M H ₂ SO ₄ , W is Pt, I		140	
Pd (II)	Palladium alloys	0.05 mg	0.55	1 M Na ₂ HPO ₄ +0.5 M H ₃ PO ₄ . W is Pt, I		142	
	Layers of a metal deposited on a copper plate	Milligram quantities	-0.80	KCN solution, W is Hg, I		143	
Ag (I)	Model solutions	Trace quantities	0.55	1 M HClO ₄ , W is Au, L. Au interferes		141	
	Pd alloys	Microgram quantities	-0.15	0.1 M NH ₄ Cl+0.1 M NH ₄ OH, W is Pt, I		142	
Ag (I)	Solutions	4 mg	-0.05, (-0.10)-(-0.15)	0.4-0.5 M HClO ₄ or HNO ₃ , W is Pt, Au, L. Fe(III) interferes		246, 235	
	Alloys	Milligram quantities	0.00	1 M HClO ₄ , W is Hg, I		144	
	Standard solutions	Milligram quantities	-0.89	0.5 M ammonium tartrate + 0.35 M NH ₄ OH, pH 9, W is Hg, I		145, 236	
	High purity Zn, solder	Trace quantities	-0.75	0.1 M KNO ₃ , containing ¹⁰⁹ Cd, W is Hg, I		146	
Cd (II)	Alloys	Milligram quantities	-0.63	1 M HClO ₄ , W is Hg, I		144	
	Standard Samples	Milligram quantities	-0.73	0.1 M KNO ₃ , W is Pt, Hg, I		147, 148	

	Solutions	1.10 ⁻⁴ —1.10 ⁻³ M	-1.10	0.1 M KCl, W is amalgamated Ag, I	149
		1.10 ⁻⁴ M	0.9	0.1 M HCl, pH 1, W is a fine mercury film on Ag backing, I	150
In (III)	Ag-In-Cd alloys	Milligram quantities	-0.62	1 M HClO ₄ + 1 M NaI, W is Hg, I. Ag(I), Cd(II) interfere	144
Sn (IV)	Alloys	0.1—0.4 mg	-0.29	3 M KBr + 0.2 M HBr, W is Hg, I. Cd(II), Pd(II) interfere	145
Te (IV)	Model solutions	0.02—1.0 mg	-0.6; -0.9 or -0.55	Phosphate buffer (pH 5.9), acetate buffer (pH 4.1), ammonia buffer (pH 9), W is Au or amalgamated Au, I	135
Ba (II)	Barium(II) salt solutions, eluate	0.4—1.4 mmole	-2.0	0.5 N (C ₂ H ₅) ₄ NI, W is Hg, I	32, 115, 116, 151
Eu (III), Sm (III), Nd (III), Yb (III)	Standard solutions	1 mg-eq	-1.30; -1.70; -2.20	0.01 M tetraethylammonium perchlorate in acetonitrile, W is Hg, I	152
Eu (III)	Eu-Cd alloys	0.26—0.86 mg	-0.30	Eu(III)→Eu→Eu(III), W is Hg, I	153
Re (II), W (III)	Alloys (Re-Mo, Re-W)	0.7—80.0 mg	0.40	2 M NaOH, W is metal alloy, I	154
	Model solutions	10 mg	0.32	0.2 M HCl, W is Pt, I	155
Ir (IV)	Concentrates after removal of precious metals	Milligram quantities	0.25	0.2 M HCl, W is Pt, I	141
Pt (II)	Pd Alloys	Milligram quantities	-0.19 or 0.55	0.1 M NH ₄ Cl+0.1 M NH ₄ OH, 1 M Na ₂ HPO ₄ + 0.5 M H ₃ PO ₄ , W is Pt, I	142
	Pd Alloys	Milligram quantities	0.55	1 M Na ₂ HPO ₄ + 0.5 M H ₃ PO ₄ , W is Pt, I	142
Au (III)	Metal layers deposited on a copper plate	Milligram quantities	-1.0	KCN solution, W is Hg, I	143
Hg (II)	Model solutions	4.10 ⁻⁴ —4.10 ⁻³ M	0.80	0.1 M HClO ₄ , W is glassy graphite, I	156
Pb (II)	Model solutions	1.10 ⁻³ M	0.90	0.1 M HCl, pH 1, W is a thin mercury film on Ag backing, I	150
Rb (IV)	Lead salts	Microquantities	0.4—0.6	HNO ₃ solution, W is Pt, I	157
	Galenite	20 mg	0.9	Pb(II)→PbO ₂ →Pb(II), 1.5M HNO ₃ , W is Pt, I = 15 mA/cm ² , t = 20°C	242
PbO	Zn, Pb	3.10 ⁻³ %	-1.6	3 M HClO ₄ , W is amalgamated lead, I	158

Table 1. (Continued)

Determined component	Analyzed object	Determinable amounts	Potential of the working electrode, rel. s.c.e.	Experimental conditions. Interfering ions	Literature
1	2	3	4	5	6
Pb (II)	Model solutions	10^{-3} — 10^{-7} mole/liter	-0.65	0.1 M HClO ₄ , W is glassy graphite, I. Cu(II) interferences	159
	Glasses, standard solutions	Milligram	-0.15	Pb(II)→Pb(Hg), 0.4 M C ₄ H ₄ O ₆ +0.30-0.70 M HClO ₄ , W is Hg, I	160
Pb (II)	Alloys, standard samples	Milligram	-0.55	3 M NaBr+0.25 M C ₄ H ₄ O ₆ , W is Hg, I	160
		$5 \cdot 10^{-4}$ — $7 \cdot 10^{-7}$ M	(-0.80)—(-0.0)	Pb(II)→Pb(metal), 0.1M NaClO ₄ , pH 2, W is carbon pyroceramic	161
Bi (III)	Standard solutions, glasses	Milligram quantities	0.19	Bi(III)→Bi(Hg), 0.4M C ₄ H ₄ O ₆ +0.1M HClO ₄ , W is Hg, I	160
Po (II)	Standard solutions	0.4—8.0 mg	-0.84	0.1 M HClO ₄ , W is Au, I	162
	U—Al alloys	~24%	-0.15	U(VI)→U(IV), H ₂ SO ₄ , W is Hg, I	163
U (VI)	Uranium standards	33—114 mg	-0.79	0.25 M H ₂ SO ₄ , W is Hg, I	164
	Uranium—neptunium alloys	Milligram quantities	-0.33	0.05M H ₂ SO ₄ +0.5M sulfanilic acid, W is Hg, I. Sb, Bi, Sn, Mn interfere	165
	Uranyl nitrite solutions	150—300mg	0.15—0.20	U(VI)→U(IV), 4.5M HCl+1.5M sulfanilic acid, W is Pt, I. Fe(III), Pu(IV) interfere	166
	Uranium oxides	Milligram quantities	-0.38	U(VI)→U(IV), H ₃ PO ₄ , W is Hg, I	167
	Mixture of U and Pu oxides	Milligram quantities	0.15	U(VI)→U(IV), 0.5M H ₂ SO ₄ +0.3M H ₃ PO ₄ , W is Hg, I	168
U (IV)	ThO ₂ and UO ₂ mixture, synthetic mixtures, UO _{2+x} samples, uranium oxides, fuel for nuclear reactors	0.2—20.0 mg	(-0.24)—(-0.38)	30% H ₃ PO ₄ , 0.5M H ₂ SO ₄ +6M H ₃ PO ₄ , 6M H ₃ PO ₄ +1M HClO ₄ , 0.5-1.0M H ₂ SO ₄ , 5M H ₂ SO ₄ , W is Hg, I	169—174
	Ceramic oxides of nuclear combustible	0.2-20.0 mg	-0.35	U(IV)→U(VI), 1M H ₂ SO ₄ , W is Hg, I	175
	Mixture of uranium and plutonium oxides	Milligram quantities	0.72	0.25M H ₂ SO ₄ +1M HNO ₃ , W is Au, I	176, 177

Np (IV)	U-Np mixture	Milligram quantities	1.02	0.5M H ₂ SO ₄ containing 0.25 ml of 0.05 Ce(SO ₄) ₂ and 0.5 ml of sulfanilic acid, W is Pt, I. Au, Hg, Te, Cl ⁻ (0.1 M) interfere	165
Np (V)	Standard solutions	Milligram quantities	-0.70	1M H ₂ SO ₄ , W is glass, I	126, 178
	Pu-containing materials, solid and liquid samples	1-2 mg	0.7	Pu(IV)→Pu(III), 1-5M H ₂ SO ₄ , W is Pt, I. U(IV) interferes	172, 179
	Mixture of uranium and plutonium oxides	2.6 mg/ml	0.32	0.25M H ₂ SO ₄ + 1M HNO ₃ containing 1 ml of sulfanilic acid, W is Au, I	176
	Ceramic fuel materials	Milligram quantities	0.95	Pu(IV)→Pu(III), 1M H ₂ SO ₄ , W is Pt, I	179
Pu (IV)	Mixture of uranium and plutonium	0.2-25 mg	0.30	0.05-0.4N H ₂ SO ₄ + 0.03N benzophenanthroline-sulfonic acid disodium salt; 0.5M H ₂ SO ₄ containing sulfanilic acid, W is Hg, I	180, 181
			0.70; 0.30	Pu(IV)→Pu(III), 1M H ₂ SO ₄ 1M HCl + 7·10 ⁻² M sulfanilic acid, W is Pt, I	182
			0.93	Pu(IV)→Pu(III), 0.5M H ₂ SO ₄ + 0.3M H ₃ PO ₄ , W is Pt, I. Nitrogen oxides, indium, mercury interferes	126, 168 183, 184
			0.55	Pu(IV)→Pu(III), 4M HCl + 2M H ₂ SO ₄ , W is Pt, I	126, 130, 182, 185, 186
	Uranyl nitrate solutions, reprocessing products of irradiated nuclear fuel, Pu(IV) oxides	Milligram quantities		Pu(IV)→Pu(III), 4M HCl + 2M H ₂ SO ₄ , W is Pt, I	
	Eluate	21-23 mg	0.74	0.5M H ₂ SO ₄ , W is glassy graphite, I	132
Pu (III), Pu (IV)	Mixtures of U and Pu oxides	Milligram quantities	0.35; 0.93	0.5M H ₂ SO ₄ + 0.3M H ₃ PO ₄ , W is Pt, I	168
Pu (IV)	Plutonium oxides, 15% metal/ceramic	1-10 mg	0.22; 0.70	Pu(IV)→Pu(III)→Pu(IV), 0.5M H ₂ SO ₄ , W is Pt, I	174, 182, 238, 243
Am (III)	Model solutions	400-1300 mg	1.05	Am(III)→Am(VI), 0.05-0.2% AgNO ₃ + (NH ₄) ₂ S ₂ O ₈ , W is Pt, I	187

TABLE 2. Direct Coulometry ($i = \text{const}$). Accepted abbreviations: i is the value of electrolysis current, Q_c is the content of material calculated from the amount of electricity consumed for electroresolution from the surface of the working electrode of metal ion removed preliminarily from the analyzed solution, W is the working electrode, A is the auxiliary electrode, $\rightarrow$ is transfer of the material from one phase to another.

Determined component	Analyzed object	Determinable amounts	Experimental conditions, electrolysis current	Literature
1	2	3	4	5
H_2	Steels	Microquantities	C_2H_5OH containing 50 ml of HCl and 25 ml of $C_4H_9O_6$ or CH_3OH containing 50 ml of 2M HCl and 2.5 g of citric acid, W is Pt	188
H_2, H_2O	Organic and inorganic materials	1.0–1.5 mg	15% H_3PO_4 , W is Pt, A is Pt, $i \leq 36$ mA	189
O_2	Copper oxide	20%	$2CuO \rightarrow 2Cu + O_2$, 1.5M $NaOH$, i 10 mA, W is amalgamated Pt, A is Pt	190
	Organic materials	1.0–1.5 mg	Organic material, $CO \rightarrow CO_2 \rightarrow H_2O$, i 10 mA, W is Pt, coated with P_2O_5 , A is Pt	191
Ni (II)	Metals, alloys, solder based on Ag, Cu	8 $\mu g/ml$	$Ni(II) \rightarrow Ni \rightarrow Ni(II)$, 0.05M $H_2SO_4 + 0.05M K_2SO_4$, 0.05M $NH_4OH + 0.05M (NH_4)_2SO_4$, W is C, Pt, Q_c	192, 193
	Brasses	0.1 mg/ml	$Cu(II) \rightarrow Cu \rightarrow Cu(II)$, 0.1M $H_2SO_4 + 0.1M K_2SO_4$, W is Pt, C, Q_c	194
	Electrolyte solutions	Milligram quantities	$Cu(II) \rightarrow Cu \rightarrow Cu(II)$, W is Pt	195
Cu (II)	Bronzes, Cu–Ni, Ag–Ni–Cu, Cd–Cu, Ag–Cu–Bi solders, solders based on Cu, Zn, Mg, Al, Sn, Fe	$\geq 1 \mu g/ml$	$Cu(II) \rightarrow Cu \rightarrow Cu(II)$, 0.05M $H_2SO_4 + 0.05M K_2SO_4$, 0.05M $NH_4OH + 0.05M (NH_4)_2SO_4$, W is Pt, C, Q_c	196, 206, 234
	Semiconductor compounds, alloys based on Se, Te, Ag, Cu	$\geq 1 \mu g/ml$	$Cu(II) \rightarrow Cu \rightarrow Cu(II)$, 0.05M $H_2SO_4 + 0.05M K_2SO_4$, ethanol, 0.1M $KCl + 0.1M HCl$, W is Pt, C, Q_c	199–207
	Ag–Cu alloys	$\geq 5 \cdot 10^{-3}$ g	$Cu(II) \rightarrow Cu \rightarrow Cu(II)$, 1 g of $(NH_4OH)_2SO_4 + 1$ ml of H_2SO_4 in 1 liter of H_2O , W is Pt, i 2.5–5.0 mA/cm ²	240
Zn (II)	Brasses, electrolyte solutions, galvanic vats	$> 8 \mu g/ml$	$Zn(II) \rightarrow Zn \rightarrow Zn(II)$, 0.05M $NH_4OH + 0.05M (NH_4)_2SO_4$, 0.1M $H_2SO_4 + 0.1M K_2SO_4$, W is C, Pt, Q_c	194, 208, 209
Se (IV)	Model solutions, alloys, semiconductor compounds, sludges, compounds on Se, Cu, Te, and Ag	$> 8 \mu g/ml$	$Se(IV) \rightarrow Se \rightarrow Se(IV)$, aqueous and alcohol solutions containing 0.1 M KCl , W is copper-plated Pt, C, Q_c	210–213
Mo (VI)	Electrolyte solutions	10^{-6} mole/liter	$Mo(VI) \rightarrow MoO_2 \rightarrow Mo(VI)$, Citric acid solution, W is Hg	214

	Galvanic coatings, microresistors	Milligram quantities	0.05M H ₂ SO ₄ +0.05M K ₂ SO ₄ . W is analyzed object, i ≥ 1 mA. HNO ₃ , SAM interfere	215
Ag (I)	Alloys, Ag-Cu, Ag-Cu-Cd, Ag-Cu-Ni, Ag-Bi, Ag-Cu-Bi, Ag-Se-Te	> 8 µg/ml	Ag(I)→Ag→Ag(I), 0.05M H ₂ SO ₄ +0.05M K ₂ SO ₄ +K ₂ S ₂ O ₈ , 0.05M NH ₄ OH+0.05M (NH ₄) ₂ SO ₄ +(NH ₄) ₂ SO ₄ . W is Pt, C. Qc	192, 193, 196-199, 216-221, 234
	Ag oxide or hydroxide, silver salts	Milligram quantities	1.3-2.0M NaOH, i 20-200 mA, W is Ni	232
	AgNO ₃ solutions	0.2-1.2 mg	0.1M HClO ₄ , i 2 mA, W is Pt	233
	Semiconductor compounds Ag ₃ SI, Ag ₃ SBr	> 30%	i 0.05 mA. W is Ag ₃ SBr or Ag ₃ SI	234
Cd (II)	Electrolytes, alloys, solders based on Cd-Cu, Ag-Cd-Cu, Ag-Cu-Cd-Ni	> 8 µg/ml	Cd(II)→Cd→Cd(II), 0.05M H ₂ SO ₄ +0.05M K ₂ SO ₄ , 0.05M NH ₄ OH+0.05M (NH ₄) ₂ SO ₄ . W is Pt, C. Qc	197
Te (IV)	Model solutions, sludges, alloys, semiconductor, compounds based on selenium, tellurium, silver, copper	> 8 µg/ml	Te(IV)→Te→Te (IV), 0.05M H ₂ SO ₄ +0.05M K ₂ SO ₄ , 0.1M HNO ₃ +0.1M KNO ₃ , 0.1M HCl+0.1M KCl, ethanol containing 0.1M KCl+0.1M HCl. W is Pt, C. Qc	213 212
Au (III)	Electrolytes, A-S-Ag alloys	> 8 µg/ml	Au(III)→Pu→Pu(III), 0.15M KCN+0.02M K ₂ SO ₄ +0.05M K ₂ SO ₄ . W is Pt, C. Qc	225, 226
Pb (II)	Electrolytes	Milligram quantities	Pb(II)→Pb→Pb(II), 70g/liter of NaOH, 1g/liter of NH ₄ OH, HCl and 20 g/liter of glycerin. W is stainless steel	227
Bi (III)	Model solutions, alloys, Ag-Bi-Cu, Ag-Bi solders, BiT ₃ monocrystal	> 8 µg/ml	Bi(III)→Bi→Bi(III), 0.1M HNO ₃ +0.1M KNO ₃ , W is Pt, C. Qc	228, 229 234
U (VI)	Pure uranium, oxides	Milligram quantities	U(VI)→U(III)→U(IV)→U(VI), 1M HCl, i 10 mA. W is Pt	230
Pd (IV)	Model solutions	Milligram quantities	Pd(IV)→Pd, 10% H ₂ SO ₄ (boil.), 10% HCl, i 3-4 mA/cm ² . W is Pt	231

nonaqueous solvent and fusions.

The use of DC, particularly at $E = \text{const}$, is also promising for standardization of metal ion solutions in non-aqueous media, determination of solution products of chemical current sources, and clarification of the degree of deterioration of metallic components in petroleum products. The method gives great possibilities for establishing the stoichiometric composition of semiconductor compounds, the ionic state of an element, products of radioactive transformations, and control of content and distribution of impurities in natural objects.

The DC variant with $i = \text{const}$ (substoichiometric coulometry) is promising for use in the determination of the thickness of a galvanic coating, composition of two-, three-, and four-component solders, analysis of stoichiometric semiconductor compounds, and the composition of galvanic vats.

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