염기성 수용액에서 우라닐이온의 전기화학적 환원

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Electrochemical Reduction of Uranyl Ion in Aqueous Basic Solutions

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요 약. 우라닐 이온의 염기성수용액에서의 전기화학적인 환원 반응을 폴라로그래피 및 순환전압 전류법을 써서 고찰하였다. 그 결과 0.1M 탄산수소나트륨 및 여기에 0.1M sodium tripolyphosphate 를 섞은 혼합용액에서 첫째 환원파는 UO_2^{2+}로 부터 UO_2^+로 환원반응이 일어난 결과로 볼수 있다. 또한 우라닐이온은 이매질에서 상당한 정도의 가수분해가 일어난 것으로 안다. 이 가수분해 생성물 인 UO_2OH^+는 첫째환원파에서 환원이 일어나지 않고 둘째 환원파에서 UO_2^+와 함께 일어난다. 우라 닐이온 농도 7.5×10^{-4}에서 3.75×10^{-3}M 까지의 범위에서 확산전류는 비례관계가 성립한다.

ABSTRACT. The electrochemical reduction of uranyl ion in aqueous basic media has been examined by d.c. polarography, differential pulsed polarography and cyclic voltammety. From voltammograms obtained in uranyl solutions containing 0.1M sodium bicarbonate, either with or without the same amounts of sodium tripolyphosphate it is concluded that the first wave corresponds to the reduction of UO_2^{2+} to UO_2^+. It is assumed that the uranyl ion undergoes appreciable hydrolysis in these media. The hydrolysis product UO_2OH^+ from UO_2^{2+} is not reduced at the first wave, but is reduced at the second wave together with UO_2^+. The diffusion current was found proportional to the uranyl concentration in a range between 7.5×10^{-4} and 3.75×10^{-3}M.

INTRODUCTION

The reduction of U(VI) has been extensively studied in aqueous media by different electrochemical methods. Most of these studies have been carried out in acidic ($HClO_4$, HCl, H_2SO_4, HNO_3) media. In sufficient acidic solution, the reduction mechanism[1~3] is that uranyl ion undergoes a one electron reduction and the resulting U(V) species disproportionates, regenerating U(VI). The disproportionation rate has been found to be first order in H^+ concentration according to the rate law[4~6]

$$-d[UO_2^+]/dt = k[UO_2^+]^2 [H^+]$$

A portion of the U(VI) from the disproportionation reaches the electrode and is reduced. The limiting current therefore has a reaction-controlled as well as a diffusion-controlled component. In less acidic solutions (above pH 3) the situation is simplified because the disproportionation of U(V) does not take place[7], but studies in weakly acid to neutral aqueous media[7,8] are few. Polarographic study of uranium is also

beset with the phenomenon of hydrolysis. Uranyl ion hydrolyzed[9] even at pH 3.0. Therefore, the investigations so far are limited primarily to the acidic side. The study of the complexes at higher pH is further complicated by the fact that not only the uranyl ion hydrolyzed, but also the complex species. However, according to Ahrland[9], complexes still can be studied under these circumstances, since the complexes are generally hydrolyzled to a less extent than the uncompexed species, because the former have less ionic charge and fewer places of coordination for hydrolysis to occur. Aqueous carbonate solutions, in spite of their great interest in nuclear technological processes, are not extensively used as supporting electrolytes for the U (VI) reduction studies. Nevertheless the analytical application of polarography in carbonate solution is a well known technique for the quantitative determination of U(VI)[10, 11]. Hagiwara[11] found that proportionality between diffusion current and UO_2^{2+} concentration in the range of $0.5 \times 10^{-3} - 3.0 \times 10^{-3}$M in potassium bicarbonate solution and recommended the carbonate solution as the supporting electrolyte for the polarographic determination of U(VI). The behavior of some tripolyphosphate complexes at the dropping mercury electrode has been examined[12], in particular that of the uranyl tripolyphosphate complex. Frankenthal and Neuberg[13] were the first to report on the interesting masking effects of sodium tripolyphosphate. Feigel[14] later observed that this reagent was far more effective in masking inorganic precipitations than any known at the time.

In this work we have studied the electrochemical behavior of uranyl in sodium bicarbonate and in sodium bicarbonate-sodium tripolyphosphate solutions. The measurements were performed using D.C. polarography, differential pulse polarography (DPP) and cyclic voltammetry.

EXPERIMENTAL

The polarographic behavior (DC and DPP) was studied using a PAR Model 174-A Polrographic analyzer and PAR Model 303 static mercury drop electrode. A Shimazu RP-50 Polarograph was also utilized to obtain wave height of the polarograms. The electrochemical cell was a PAR Model 9300~9301 polarographic cell employed in a three electrode configuration. The auxiliary electrode was a platinum wire (1.5mm in diameter and 5cm long) and the working electrode was a dropping mercury electrode. The working electrode was set up using triply-distilled mercury. The reference electrode was saturated silver/silver chloride or SCE, as indicated. All values of potential in this work are with reference to this SCE.

The cyclic voltammetry was performed with a PAR Model 173 potentionstat/galvanostat coupled to a PAR Model 175 universal programmer. The working electrode in the cyclic voltammetric experiments was a PAR Model 9323 hanging mercury drop electrode. The polarogramms and the cyclic voltammograms at slow scan rates were recorded with an x-y recorder (Moseley Model 2D-2M). The pH-values of the solution were measured using a Philips PW409 digital pH-meter.

Before electrolysis, all solutions were purged with purified presaturated wet nitrogen for at least 15min and blanketed with it during the run. Analytical reagent grade uranyl nitrate, sodium bicarbonate and sodium tripolyphosphate were used without further purification. The experiments were carried out at 25°C.

RESULTS AND DISCUSSION

Polarographic behavior of uranyl ion in 0.1M sodium bicarbonate(I) and in sodium bicarbonate-sodium tripolyphosphate (STP) (II) solution

showed two-step waves corresponding to U(VI) →U(V) and U(V)→U(IV) respectively. The wave heights and half-wave potentials vary with the concentrations of I and II. In both solutions the first wave is well defined, but the second wave is not. In I-II solution, each 0.1M (pH8.3.) the half-wave potential shifted towards more positive potentials. Reversibility of the electrode reaction was checked by the Tomes equation[15], as shown in *Table* 1. The value of $E_{3/4}-E_{1/4}$ for the first wave, -118 and -86mV, suggested the reduction wave is probably irreversible. The logarithmic analysis of the first wave gave a straight line with a slope of 0.133 and 0.109V, as expected for an irreversible one electron process.

As shown in *Table* 2 the wave height of the first wave varied with the square root of the head of the dme and was found constant in $i_d/h_{corr.}^{1/2}$ suggesting that this electrode reaction was diffusion-controlled and not rate-controlled. The temperature coefficient of the diffusion current has also been employed to check the electrode reaction. The average value, 1.52% /°C which also indicated diffusion-controlled reaction (*Table* 3).

The dependence of diffusion-current and half-wave potential on the pH value was determined by polarographing a solution of 1.5×10^{-3}M uranyl nitrate in 0.1M NaHCO$_3$ at various pH values. The diffusion current decreased with the increase of pH value, but no linear relation was found (*Fig.* 1). The effect of pH on the half-wave potential is also shown in *Fig.* 1. The independency of the half-wave potentials of the acidity indicates that hydrogen ions are not involved in the electrode reactions.

The diffusion current was measured by varying the uranyl ion concentration from 7.5×10^{-4}M to 3.75×10^{-3}M in 0.1M NaHCO$_3$ and in 0.1M NaHCO$_3$- 0.1M STP at pH 8.30 (*Table* 4).

Table 1. Polarographic characteristics of uranyl ion[a]

Supporting electrolyte	$E_{1/2}$ (V $vs.$ SCE)	I[b]	$E_{3/4}-E_{1/4}$[c]
0.1M NaHCO$_3$	-1.14, -1.60	1.66	118
0.1M NaHCO$_3$ +0.1M STP	-1.08, -1.53	1.66	86
0.1MSTP	-1.81[d]		

[a] test solutions contained 1.0×10^{-3}M uranyl ion
[b] diffusion current constant for the first wave
[c] in mV for the first wave
[d] potential for the reduction of Na$^+$ ion.

Table 2. Variation of diffusion current[a] with mercury pressure

h(cm)	t(sec)	m(mg/sec)	$i_d(\mu A)$	$i_d/h_{corr.}^{1/2}$
47	5.29	0.912	3.2	0.467
52	4.54	1.037	3.4	0.465
57	4.12	1.140	3.5	0.464
62	3.62	1.296	3.7	0.469
67	3.54	1.339	3.8	0.464

[a] the first reduction of U(VI)
test solution contained 1.0×10^{-3}M UO$_2^{2+}$ and 1.0M NaHCO$_3$.

Table 3. Relationship between diffusion current[a] and temperature

Temp. (°C)	$i_d(\mu A)$	Temp. coeff. (%/°C)
16	3.3	
20	3.5	1.52
25	3.8	1.52
30	4.0	1.52

[a] the first reduction of U(VI)
test solution contained 1.0×10^{-3}M0UO$_2^{2+}$ and 1.0M NaHCO$_3$.

In this concentration range the diffusion current is proportional to concentration within the experimental error, ca. 1 to 2%. It is evident that the supporting electrolytes, I and I-II are recommended as supporting electrolytes for the polarographic determination of uranium (VI) because the diffusion current is proportional to the concentration.
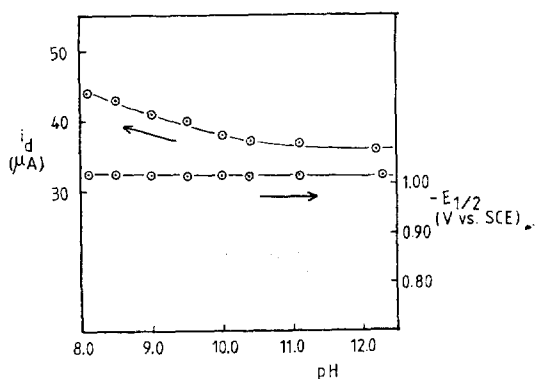
Fig. 1. Effect of pH on half-wave potential and diffusion current of the first reduction of U(VI). UO_2^{2+}: 1.0×10^{-3}M, $NaHCO_3$: 0.1M, pH: adjusted with NaOH.

Table 4. Diffusion current[a] as a function of uranyl ion concentration

UO_2^{2+} concn. (M)[b]	$i_d(\mu A)$	$i_d/C(\mu A/mM)$
7.5×10^{-4}	2.0	2.66
1.5×10^{-3}	3.9	2.60
2.25×10^{-3}	5.9	2.62
3.0×10^{-3}	8.0	2.66
3.75×10^{-3}	10.0	2.66

[a] the first reduction of U(VI). [b] contained 1.0M $NaHCO_3$. pH:8.3 (adjusted with NaOH)

UO_2^{+2} concn. (M)[b]	$i_d(\mu A)$	$i_d/C(\mu A/mM)$
7.5×10^{-4}	25.0	33.2
1.5×10^{-3}	50.0	33.3
2.25×10^{-3}	75.0	33.3
3.0×10^{-3}	100.0	33.3
3.75×10^{-3}	125.0	33.3

[a] the first reduction of U(VI). [b] contained 0.1M $NaHCO_3$ and 0.1M STP. pH: 8.3(adjusted with NaOH).

The effect of sodium bicarbonate and STP concentration on the half-wave potential and diffusion current was studied by varying the concentration of the supporting electrolytes and keeping the concentration of uranyl ion constant at 1.0×10^{-3}M. The results are shown in Table 5 and Fig. 2, in which the half-wave potential is plotted against the logarith of sodiumm

Table 5-1. Effect of sodium bicarbonate concentration upon the half-wave potential of the first reduction of U-(VI)[a]

$NaHCO_3$(M)	$E_{1/2}$(V vs. SCE)	$i_d(\mu A)$
0.001		
0.002		
0.003		
0.004		
0.005		
0.01	−1.62	45.2
0.05	−1.35	84.4
0.10	−1.15	88.5
0.50	−1.08	91.0
0.80	−1.03	89.2
1.00	−1.01	84.6
1.20	−1.00	87.0

[a]. test solution contained 1.0×10^{-3}M.

Table 5-2. Effect of concentration of sodium bicarbonate and STP upon the half-wave potential of the first reduction of U(VI)[a]

$NaHCO_3$(M)	STP(M)	$E_{1/2}$(V vs. SCE)	$i_d(\mu A)$
0.001	0.001	−1.64	17.0
0.002	0.002	−1.63	26.6
0.003	0.003	−1.63	47.0
0.004	0.004	−1.61	60.2
0.005	0.005	−1.57	62.0
0.006	0.006	−1.53	66.6
0.007	0.007	−1.51	68.0
0.008	0.008	−1.48	75.4
0.009	0.009	−1.46	81.6
0.01	0.01	−1.46	81.8
0.05	0.05	−1.23	93.0
0.10	0.10	−1.09	86.2
0.50	0.50	−0.95	47.6
0.80	0.80	−0.92	47.0
1.00	1.00	−0.89	40.8
1.20	1.20	−0.86	33.6

[a] test solution contained 1.0×10^{-3}M.

bicarbonate or STP concentration. As shown in Fig. 2, the curve can be seen to be formed by the superimposing of two straight lines showing the formation of two complexes. The two breaks, therefore indicate that the uranly ion probably forms with tripolyphosphate complex in
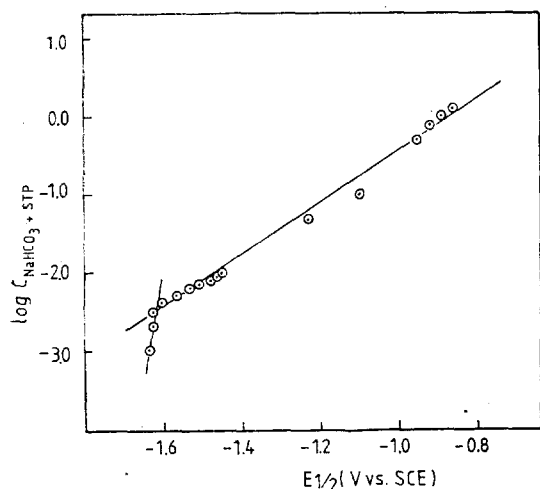
Fig. 2. Variation of half-wave potential as a function of sodium bicarbonate–STP concentration.

Table 6. Cyclic voltammetric data[a] for the reduction of U(VI)[b]

scan rate(v) (mV/sec(	E_p (V $vs.$ SCE)	i_p (μA)	$i_p/v^{1/2}$ (μAmV$^{-1/2}$sec$^{1/2}$)
20	−1.36	31.2	7.0
50	−1.38	44.6	6.3
100	−1.43	60.1	6.0
200	−1.61	81.0	5.7
500	−1.60	115.0	5.1

[a] Data for the first sweep. The working electrode was a hunging mercury drop electrode, auxiliary electrode was platinum wire and aqueous SCE was used as a reference electrode.
[b] The solutions contained 1.0×10^{-3}M and 0.1M NaHCO$_3$.

scan rate(V) (mV/sec)	E_p (V $vs.$ SCE)	i_p (μA)	$i_p/v^{1/2}$ (μA mV$^{-1/2}$sec$^{1/2}$)
20	−1.26	46	10.3
50	−1.28	62	8.8
100	−1.30	79	7.9
200	−1.37	108	7.6
500	−1.46	145	6.5

[a] Data for the first sweep.
[b] The solutions contained 1.0×10^{-3}M and 0.1M NaHCO$_3$−0.1M STP.

addition to uranyl tricarbonate complex.

The discrepancy in diffusion currents which

Table 7. Cyclic voltammetric results

UO$_2^{2+}$ concn.[a] (mole/liter)	i_p (uA)	E_p (V $vs.$ SCE)	$i_p/v^{1/2}C^{ob}$ (μA mM^{-1} mV$^{-1/2}$sec$^{1/2}$)
1.0×10^{-3}	62	−1.45	6.2
2.0×10^{-3}	107	−1.45	5.4
3.0×10^{-3}	164	−1.45	4.8
4.0×10^{-3}	223	−1.45	5.6
6.0×10^{-3}	328	−1.45	5.5
8.0×10^{-3}	435	−1.45	5.4
10.0×10^{-3}	465	−1.46	4.7

[a] Test solutions contained 0.1M NaHCO$_3$.
[b] Scan rate was fixed at 100 mV/sec.

UO$_2^{+2}$ concn.[a] (mole/liter)	i_p (μA)	E_p (V $vs.$ SCE)	$i_p/v^{1/2}C^{ob}$ (μA mM^{-1} mV$^{-1/2}$sec$^{1/2}$)
1.0×10^{-3}	82	−1.30	8.2
2.0×10^{-3}	142	−1.30	7.1
3.0×10^{-3}	194	−1.30	6.5
4.0×10^{-3}	250	−1.30	6.3
6.0×10^{-3}	370	−1.30	6.2
8.0×10^{-3}	460	−1.30	5.8
10.0×10^{-3}	570	−1.30	5.7

[a] Test solutions contained 0.1M NaHCO$_3$ −0.1M STP
[b] Scan rate was fixed at 100 mV/sec.

listed in *Table* 4 and 5 was due to the utilization of two different types of polarograph. The cell used in the Shimazu RP-50 polarograph was an H type with two-electrode system, whose maximum current-sensitivity was lower than PAR Model 303 SMDE.

Triangular sweep cyclic voltammetry of 1.0×10^{-3}M uranyl ion in 0.1M NaHCO$_3$ and in 0.1 M NaHCO$_3$−0.1M STP solutions at a hanging mercury drop cathode yielded the results shown in *Table* 6 and *Table* 7. When the scan direction was reversed 60mV past the first cathodic peak (switching potential, $E_\lambda = -1.70$V), no oxidation peak corresponding to the reoxidation of the product of the first cathodic process was observed (*Fig.* 3). From examination of cyclic voltammograms as a function of sweep rate from 20 to 500 mV/sec using x-y recording current
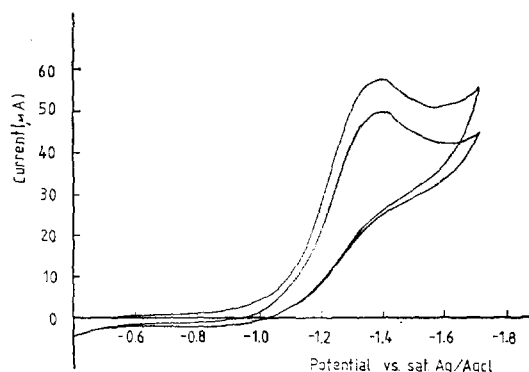
Fig. 3. Cyclic voltammetry of uranyl(VI). UO_2^{2+}: 1.0 ×10^{-3}M, $NaHCO_3$: 0.1M. scan rate(v): 100mV/sec, switching potential (E_λ): −1.70V.

function (proportingal to $i_p/v^{1/2}$) is found to decrease as the sweep rate is increased (*Table* 7). This fact may indicate a chemical reaction coupled with the electrochemical reaction at these sweep rates. The current function is defined as i_p/nFA $(Da)^{1/2}C^0$ where i_p is the peak current, v is the sweep rate, C^0 is the initial concentration of electroactive species, and the parameter is defined as $a=nFv/RT$. The factor $i_p/v^{1/2}$ C^0 in cyclic voltammetric experiments for the first wave decreased when the concentration of uranyl ion in the solution was decreased (*Table* 7). A plot of the $i_p/v^{1/2}C^0$ *vs.* uranyl concentration which contained 0.1M sodium bicarbonate and 0.1M STP for the wave shows that the first three points fall on a straight line of negative slope and the second four points fall on another similar line. The discontinuity between the third and fourth points is present in the data for the peak and appears, therefore to be an artifact of undetermined origin. There is, in any event, an overall decrease in the factor $i_p/v^{1/2}C^0$ in cyclic voltammetric experiments. The cyclic voltammetry results suggest that the uranyl ion probably undergoes appreciable hydroysis in this medium.

$$UO_2^{2+}+H_2O \longrightarrow UO_2OH^+ +H^+ \qquad (1)$$
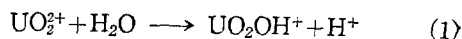
If the reduction of UO_2^{2+} to UO_2^+ is more rapid than the reestablishment of hydrolysis equilibrium according to equation (1) the magnitude of the first wave should correspond to the amount of unhydrolyzed UO_2^{2+} present in the original solution. It has been found that the hydrolysis product UO_2OH^+ from UO_2^{2+} is not reduced at the first wave[8], but is reduced at the second wave together with UO_2^-, the first wave resulting from the one-electron reduction of UO_2^{2+} alone. The UO_2OH^+ is reduced to pentavalent and not to tetravalent uranium[8].

$$UO_2OH^+ +e^- \longrightarrow UO_2OH \qquad (2)$$

The uranyl ion in alkaline tripolyphosphate medium undergoes an irreversible one-electron reduction with the $E_{1/2}$ of −1.08 and −1.53V *vs.* SCE at pH 8.3. The progressive shift in the $E_{1/2}$ s to more positive values (*Table* 1 and *Table* 5-2) in the presence of STP suggest the possibility of the formation of uranyl tripolyphosphate (UTP) complexes in the concentration range which we have studied. While the nature of the complexes in this medium seems unclear, these results indicate that the complexes are formed by one mole of the uranyl ion reacting with more than one mole of STP as the concentration is increased. A steady increase in i_d with increasing pH is also observed (*Table* 8), the reason for which is not clear. A similar observation has been reported by Senise and Delahay[16] on the polarographic reduction of thallium in a pyrophosphate medium. Greater stability of the complex in alkaline medium is apparent from the merely increasing negative values for $E_{1/2}$ with rising pH. It, therefore, appears that the polarographic reduction of UTP complex proceeds essentially to the U^{5+} stage.

The concentration of uranium in sea-water is

Table 8. Effect of pH upon the half-wave potential for the first reduction of uranyl ion[a]

pH	$E_{1/2}$(V vs. SCE)	i_d (μA)
7.80	−1.105	56.0
8.29	−1.105	54.2
8.83	−1.110	55.6
9.15	−1.115	56.8
9.58	−1.120	59.0
9.86	−1.120	59.0
10.06	−1.120	59.0
10.71	−1.120	59.0
10.98	−1.125	61.0
11.32	−1.125	61.0

[a] contained 1.0×10^{-3}M UO_2^{2+}, 0.1M $NaHCO_3$ and 0.1M STP. pH: a sindicated (adjusted with NaOH)

Table 9. Effects of foreign cations[a] on the half-wave potential or U(VI) cathodic wave

Cation(M)[b]	$E_{1/2}$ (V vs. SCE)		
	0.1M $NaHCO_3$	0.1M $NaHCO_3$	+0.1M STP
$1.0 \times 10^{-3}UO_2^{2+}$	−1.14, −1.60		−1.08, −1.53
$1.0 \times 10^{-1}Na^+$	non[c]		non
$3.0 \times 10^{-2}Mg^{2+}$	non		non
$1.5 \times 10^{-3}Ca^{2+}$	non	(ppt)[d]	non
$3.0 \times 10^{-2}K^+$	non		non
$1.0 \times 10^{-3}Sr^{2+}$	non	(ppt)	non
$3.0 \times 10^{-2}Li^+$	non		non
$4.0 \times 10^{-3}Rb^+$	non		non
$1.0 \times 10^{-3}Ba^{2+}$	non	(ppt)	non
$3.0 \times 10^{-2}Mo^{6+}$	non		non
$2.0 \times 10^{-3}Ni^{2+}$	−1.005	(ppt)	non
$1.0 \times 10^{-3}Zn^{2+}$	−1.085	(ppt)	non
$4.0 \times 10^{-3}Fe^{3+}$	non	(ppt)	−0.255, −0.800

[a] contain in sea-water. [b] contained 0.1M $NaHCO_3$ or 0.1M$NaHCO_3$+0.1M STP. [c] no reduction wave above background was observed in the potential range of −2.0V vs. SCE. [d] indicates precipitate pH: 8.3 (adjusted withNaOH).

extremely low. Values as low as 0.36 μg/1 had been obtained[17] for surface water and 0.98∼1.00 μg/1 for water samples at depths between 60 and 500m. In a subsequent paper[18], values between 2.0 and 2.2 μg/1 were noted for samples from coastal and ocean waters. Of the

trace elements present in sea-water (see Appendix), nickel and zinc ions interfere in the polarographic determination of uranium in bicarbonate medium but ferric ions interfere in bicarbonate-STP medium (Table 9). It has been found that calcium (II), strontium (II), barium (II), nickel (II), zinc (II), and iron (III) formed precipitates in sodium bicarbonate solution, however these ions are soluble in the presence of STP due to the formation of soluble complexes.

For the voltammetric determination of uranyl ion in sea-water using differential pulsed polarography or stripping voltammetry it is recommended that the first diffusion current be measured at the potential of −1.08V vs. SCE in 0.1M sodium bicarbonate −0.1M STP solution.

Appendix. Chemical concentration in sea-water[a]

Cation	Concentration (g/liter)	Molar concn. ratio
Na^+	10.77	3.7×10^7
Mg^{2+}	1.29	3.8×10^6
Ca^{2+}	0.412	7.4×10^5
K^+	0.391	7.2×10^5
Sr^{2+}	8.1×10^{-3}	6.7×10^3
Li^+	1.7×10^{-4}	1.8×10^3
Rb^+	1.2×10^{-4}	1.0×10^2
Ba^{2+}	2.1×10^{-5}	11
Mo^{6+}	1.0×10^{-5}	8.1
Ni^{2+}	6.6×10^{-6}	7.5
Zn^{2+}	5.0×10^{-6}	5.5
Fe^{3+}	3.4×10^{-6}	4.4
U^{6+}	3.3×10^{-6}	1.0

[a] Reprinted from K.K. Turekian, Handbook of Geochemistry, p.309, K.H. Wedepohl, Springer-Verlag, Berlin (1969).

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