In order to increase the sensitivity of Procedure B, volumetric flasks as small as five ml. could be used for reaction of the oxalate with ceric ion. In this case, all solutions would have to be carefully weighed, but an improvement in sensitivity by a further factor of ten should result. This would enable light intensities of the order of 1 × 10^{13} quanta/sec. to be measured to 5% or better accuracy with a one-hour exposure.

The molar extinction coefficient of the dye produced when malachite green leucocyanide is employed as an actinometer[9] is 9.49 × 10^4, and that of the ferrous–phenanthroline compound,[10] formed after photolysis of potassium ferri-oxalate, is 1.1 × 10^4. These extinction coefficients may be compared to 5.4 × 10^3 for ceric ion at 3200 Å. Thus by the spectrophotometric procedure the uranyl oxalate actinometer seems capable of a sensitivity within a factor of about twenty of that of the malachite green leucocyanide actinometer[10] and within a factor of about two of that of the potassium ferrioxalate actinometer.[11] It may be that by using a suitable, very highly colored oxidation–reduction indicator to reduce the excess ceric ion quantitatively one might further increase this sensitivity.

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[9] J. G. Calvert and H. J. L. Rechen, This Journal, **74**, 2101 (1952).

[10] C. A. Parker, *Proc. Roy. Soc.* (*London*), **A220**, 104 (1953).

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The Determination of the Bisulfate Dissociation Quotient from Potentiometric Measurements[1]

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It is desirable to have values of the bisulfate dissociation quotient in solutions of unit ionic strength to permit comparisons of the relative stabilities of cations complexed by sulfate ion. A value of 0.24 was calculated by Rabideau and Lemons[2] for the dissociation quotient of the bisulfate ion at unit ionic strength and 25° from the solubility of calcium sulfate in acid–salt solutions. Zebroski, Alter and Heumann[3] estimated the value of the acid quotient to be 0.084 ± 0.020 at an ionic strength of 2.0 from *p*H measurements of solutions of sodium sulfate, sodium perchlorate and perchloric acid.

The procedure used in this work was to measure the electromotive force of the cell: Pt, H_2; $HClO_4(c_1)$, $NaClO_4$ (c_2); $HClO_4(c_1)$, $NaClO_4(c_2)$, $Na_2SO_4(c_3)$; H_2, Pt. Because of the high ionic strengths used in this cell the calculation of the liquid junction potential is not feasible, consequently an empirical approach was adopted. The proportionality constant, *k*, in the equation

$$E = k \log[\overset{+}{\mathrm{H}}]_2/[\overset{+}{\mathrm{H}}]_1$$

relating the cell e.m.f., *E*, with the ratio of the hydrogen ion concentrations in the two cell compartments was obtained by titrating the perchloric acid in one-half of the cell with standardized sodium hydroxide which contained sufficient sodium perchlorate to maintain the ionic strength at unity throughout the titration. Only a small fraction of the total perchloric acid was neutralized in each titration. No sodium sulfate was present in the determination of the values of the proportionality constant. It was assumed that the low concentrations of sulfate and bisulfate made little contribution to the liquid junction potential in the titrations in which sodium sulfate was added to the perchloric acid–sodium perchlorate solutions. Values obtained for *k* were −0.0579 ± 0.0002, −0.0461 ± 0.0007 and −0.0175 ± 0.0004 for the 0.01, 0.10 and 1.0 *M* perchloric acid solutions, respectively.

Values of the dissociation quotient for the bisulfate ion were obtained from the variation of the cell potential as a function of the sodium sulfate concentration by the considerations

$$[\overset{+}{\mathrm{H}}]_f = [\overset{+}{\mathrm{H}}]_i\, 10^{-E/k} = [\overset{+}{\mathrm{H}}]_i\, \gamma$$

where the subscripts i and f denote the initial and final states, *E* is the cell e.m.f. and *k* is the proportionality constant

$$[\mathrm{HSO_4}^-]_f = [\overset{+}{\mathrm{H}}]_i\, R - [\overset{+}{\mathrm{H}}]_i\, \gamma = [\overset{+}{\mathrm{H}}]_i\, (R - \gamma)$$

R is the dilution ratio, $V_i/(V_i + V_{\mathrm{Na_2SO_4}})$, where *V* is the solution volume. Then

$$K = [\overset{+}{\mathrm{H}}[_f[\mathrm{SO_4}^=]_f/[\mathrm{H}\overset{-}{\mathrm{SO}}_4]_f = \{\gamma/(R - \gamma)\}\{[\overset{=}{\mathrm{SO}}_4]_i - [\overset{+}{\mathrm{H}}]_i(R - \gamma)\}$$

The mean values of the bisulfate dissociation quotient obtained in perchlorate solutions of unit ionic strength varied with the acidity. The results are 0.095 ± 0.002, 0.084 ± 0.012 and 0.30 ± 0.08 in 0.01, 0.10 and 1.0 *M* perchloric acid, respectively. The results of the titration with sodium sulfate in 0.01 *M* perchloric acid–0.99 *M* sodium perchlorate are given in Table I. Within the experimental error the values of *K* in 0.01 and 0.10 *M* perchloric

Table I

Determination of Bisulfate Dissociation Quotient in 0.01 *M* $HClO_4$–0.99 *M* $NaClO_4$

$[\overset{+}{\mathrm{H}}]$i, moles/l.	$[\overset{=}{\mathrm{SO}}_4]$i, moles/l.	*R*	*E*, volts × 10^6	γ	*K*
0.01058	2.897 × 10^{-4}	0.9998	72.1	0.9971	0.096
	5.479	.9997	133.2	.9947	.098
	1.035 × 10^{-3}	.9995	260.3	.9897	.094
	1.999	.9990	455.4	.9820	.105
	2.697	.9986	641.9	.9748	.100
	3.666	.9981	898.9	.9648	.096
	4.722	.9975	1174.3	.9543	.094
	5.463	.9971	1388.7	.9463	.092
				Mean	0.095 ± 0.002

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[1] This work was done under the auspices of the A.E.C.

[2] S. W. Rabideau and J. F. Lemons, This Journal, **73**, 2895 (1951).

[3] E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

acid solutions are equal; however, it appears that in spite of the fact that the ionic strength was held at unity, the activity coefficient product is significantly different in molar perchloric acid as compared with the more dilute acid solutions.

Experimental

The electromotive force of the cells was measured to the nearest 0.1 microvolt with a type K Leeds and Northrup potentiometer. The hydrogen used for the hydrogen electrodes was purified with alkaline permanganate, sulfuric acid, alkaline pyrogallol and heated copper. Mallinckrodt analytical reagent grade sodium sulfate was used. The sodium perchlorate was prepared by the reaction between C.P. sodium carbonate and perchloric acid. The perchloric acid was standardized against mercuric oxide. The temperature of the cells was maintained at 25.00 ± 0.05° by circulating thermostated water in the jacket of the cell container. Initially no sodium sulfate was present in the right compartment of the cell and the measured e.m.f., which should have been zero, was generally less than 20 microvolts. Two hydrogen electrodes were used in each half of the cell and these were intercompared by means of a switching arrangement. Standardized sodium sulfate solution was added in small increments from a weight buret. The solutions were stirred with magnetic stirrers and the cell e.m.f. was recorded after each addition of sodium sulfate.

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Uranium(III) Cupferrate[1]

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Uranyl ion forms an insoluble cupferron salt in neutral solution; this compound, $UO_2NH_4(Cup)_3$, is insoluble in organic solvents.[2] A second, ether- and chloroform-extractable form appears to exist in acid media, but only in small proportions in very concentrated uranium solutions.[2c] Uranium(IV) forms brown $U(Cup)_4$ which is insoluble in up to 8% sulfuric acid solution, but is quantitatively extractable into ethyl ether.[2c]

Polarographic and other studies in this Laboratory indicate the existence, also, of a very stable, ether-soluble uranium(III) cupferrate. While it has not been recognized so far as is known, there is some independent evidence both that U(III) does form a cupferrate and that this compound must be chloroform- and ether-soluble. The reported work on cupferron extraction of U(IV) has involved both the use of Jones reductors without a subsequent aeration step and extraction in the presence of liquid amalgams. The presence of some U(III) might be expected in either case and quantitative extraction of the uranium is claimed.[2c] Grimaldi[3] is one of the few authors to indicate that U(III), as well as U(IV), cupferrate is involved and that U(III) is quantitatively precipitated by cupferron in 10% hydrochloric acid.

Experimental.—Conventional polarographic techniques were employed, involving manual measurement with a Fisher Elecdropode. The polarographic cell-compartment was jacketed and thermostatically regulated at 25.0 ± 0.1°; a fritted disk and agar plug junction connected to a saturated calomel reference electrode. Distilled water and reagents of C.P. or reagent grade were employed. Oxygen removal was accomplished by purging with tank nitrogen.

Discussion.—The polarographic behavior of uranium in its various oxidation states has been very thoroughly studied and is well summarized by Rodden.[4] In general, aqueous solutions of U(VI) in dilute mineral acid exhibit the reduction pattern shown on curve ABC of Fig. 1. A medium of 0.1 N sulfuric acid and 0.1 N potassium chloride was employed in the present study. Wave A is primarily due to the one-electron reduction of U(VI) to U(V). However, the U(V) disproportionates

$$2U(V) \longrightarrow U(VI) + U(IV) \qquad (1)$$

to reform some U(VI) and to give some U(IV); consequently, the wave is larger than required for a one-electron reduction. Wave BC represents the two-electron reduction of U(V) to U(III); the intermediate (IV) stage demarcating B from C appears only at higher acidities. Wave A is always larger than B, and C(IV to III) is approximately equal to one-half of A plus B(VI to IV). In 6 N acid the B wave coalesces with A.

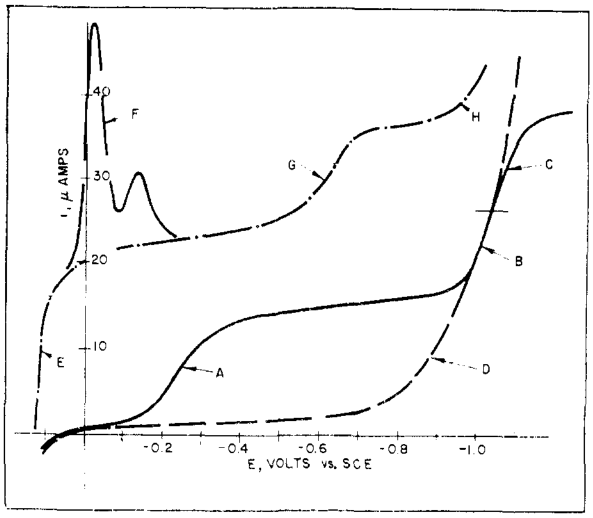

Fig. 1.—Polarographic reduction of uranium(VI) and of cupferron in dilute mineral acid solution.

Kolthoff and Liberti[5] have reported on the polarographic behavior of cupferron. The large reduction wave which occurs at more negative potentials in alkaline media, starts from about −0.8 to −0.9 v. *vs.* S.C.E. in 0.1 N acid, as shown by curve D of Fig. 1.

When a solution of 1mM uranyl ion in the presence of 10 mM cupferrate was examined, curve EFGH was obtained. The maximum at F is largely removed in the presence of 0.005% gelatin. Wave E represents the reduction of U(VI) to

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[1] This investigation was supported in part by the Air Force Cambridge Research Center under contract with the Engineering Research Institute of the University of Michigan.

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