

## VOLTAMMETRIC DETERMINATION OF IODIDE AND BROMIDE AT THE ROTATING PYROLYTIC GRAPHITE ELECTRODE

G. DRYHURST AND PHILIP J. ELVING

*The University of Michigan, Ann Arbor, Michigan (U.S.A.)*

Dedicated to Professor Dr. M. VON STACKELBERG on his 70th birthday

(Received June 1st, 1966)

Since halogens present in admixture are difficult to separate, it is desirable to be able to determine directly one halogen in the presence of others. The problem, however, of determining very low concentrations of a halide (except fluoride), especially in the presence of large excesses of other halides, has only been resolved with some difficulty.

Excellent reviews with many references on the determination of the halogens are given by KOLTHOFF AND STENGER<sup>5</sup>, and ARMSTRONG, GILL AND ROLF<sup>1</sup>. Typical of the methods described is the well-known procedure of VAN DER MEULEN<sup>7</sup> for determining bromide in the presence of chloride on a micro scale. In this method bromide is oxidized to bromate with hypochlorite and, after removal of excess oxidant, the bromate is determined iodometrically; iodide, if present, is determined as bromide and a correction must be applied by determining iodide alone. Iodide can be determined in the presence of bromide and chloride by oxidation to iodate with bromine; after removal of excess oxidant, the iodate is determined iodometrically (*cf.* refs. 1 and 5).

Polarography at the dropping mercury electrode has been used to determine the halogens in terms of the anodic waves that mercury yields in their presence<sup>1,5</sup>. However, the half-wave potentials for the waves due to chloride, bromide and iodide are so close together that the analysis of mixtures is difficult, if not impossible, especially when one of the halogens is present in excess. Polarography has been used extensively for the determination of bromide and iodide; these are first oxidized to bromate and iodate.

ELVING AND SMITH<sup>4</sup> showed that the anodic decomposition potentials of aqueous solutions of chloride, bromide and iodide were well separated at a rotating wax-impregnated spectroscopic graphite electrode. It thus seemed probable that a method for the differential determination of the halogens might be possible in terms of their differential oxidation at a graphite indicating electrode. This possibility was investigated and methods were developed for the determination of iodide and of bromide.

## EXPERIMENTAL

*Reagents*

Analytical-grade chemicals were used (J. T. Baker). Stock solutions of reagents were prepared by dissolving weighed quantities in distilled water and diluting to known volumes.

### Apparatus

All voltammograms were recorded on a Sargent Model XXI polarograph. The conventional water-jacketed H-cell<sup>6</sup> used was maintained at  $25 \pm 0.2^\circ$ ; it contained in one leg a saturated calomel reference electrode which was separated from the electrolysis compartment by a sintered disk and an agar plug saturated with potassium chloride.

The pyrolytic graphite electrode, which has now replaced the wax-impregnated graphite electrode<sup>3</sup>, was 4 mm in diameter and was prepared according to the directions given by CHUANG, FRIED AND ELVING<sup>2</sup>. The electrode was rotated at 250 rev./min by a constant-speed motor mounted on a sturdy frame. It was re-surfaced before each determination by polishing on a 600-grade silicon carbide paper mounted on a rotating disc.

A Cenco Lab-jack was used to raise and lower the H-cell in order to position the electrode.

### Voltammetric procedure

Test solutions were prepared by diluting appropriate quantities of stock solutions with suitable strength background solution.

In the early studies, purified nitrogen gas was bubbled through the test solutions before the voltammogram was taken; subsequently, this precaution was found to be unnecessary.

In order to standardize the procedure, the electrode, once positioned, was rotated for 30 sec with no applied potential; it was then rotated for a further 30 sec at the starting potential, 0.0 V *vs.* the S.C.E. Recording of the voltammogram was then commenced.

## RESULTS AND DISCUSSION

The investigations of SMITH AND ELVING<sup>4</sup> indicated that potassium sulphate might provide a suitable background electrolyte. A 0.5 M K<sub>2</sub>SO<sub>4</sub> solution had an anodic decomposition potential at the rotating pyrolytic graphite (R.P.G.) electrode of 1.30 V *vs.* S.C.E. A 0.5 M K<sub>2</sub>SO<sub>4</sub>-0.5 M H<sub>2</sub>SO<sub>4</sub> solution, however, had a somewhat larger potential range, *i.e.*, the decomposition potential was 1.6-1.7 V. When these background solutions were used, iodide showed several oxidation waves of which only the first two were reproducible and of analytical importance. Typical concentration-limiting current data for the oxidation of iodide are shown in Table I. The convenient lower limit of determination for iodide appears to be about 0.01 mM.

In acidic solution, the second iodide wave often did not appear or was very ill-defined at lower iodide concentration. However, the first wave gave reproducible  $i_l/C$ -values in both acidic and neutral solution although the wave was better shaped in acidic solution. At iodide concentrations above about 0.5 mM, both waves appeared in acidic solution and were usually well formed.

Bromide gave only one analytically useful anodic wave at the R.P.G. electrode. This wave was not as well formed as the first iodide wave; because of this the convenient lower limit of determination of bromide is about 0.1 mM. The shape of the bromide wave was also best in acidic solution. Typical concentration-limiting current data are presented in Table 2.

TABLE 1

VOLTAMMETRIC OXIDATION OF IODIDE IN SULPHATE BACKGROUND AT THE R.P.G. ELECTRODE<sup>a</sup>

Iodide concn. (mM)	Wave I			Sum of waves I and II		
	$i_1$ ( $\mu A$ )	$E_{1/2}$ (V)	$i_1/C$ ( $\mu A/mM$ )	$i_1$ ( $\mu A$ )	$E_{1/2}$ (V)	$i_1/C$ ( $\mu A/mM$ )
0.5 M K <sub>2</sub> SO <sub>4</sub>						
0.01002	0.68	0.565	68	1.40	0.750	140
0.03006	1.78	0.537	59	2.76	0.741	92
0.1002	5.55	0.528	55	9.03	0.722	90
1.002	49.8	0.505	50	88.3	0.796	88
0.5 M K <sub>2</sub> SO <sub>4</sub> + 0.5 M H <sub>2</sub> SO <sub>4</sub> <sup>b</sup>						
0.01002	0.545	0.550	54			
0.03006	1.49	0.528	50			
0.1002	4.79	0.518	48			
1.002	48.7	0.491	49	77.9	0.968	80

<sup>a</sup> Potentials are vs. S.C.E. Quoted results are average of at least two separate determinations.<sup>b</sup> At low iodide concns. a second wave often did not appear.

TABLE 2

VOLTAMMETRIC OXIDATION OF BROMIDE IN 0.5 M K<sub>2</sub>SO<sub>4</sub>-0.5 M H<sub>2</sub>SO<sub>4</sub> BACKGROUND AT THE R.P.G. ELECTRODE<sup>a</sup>

Bromide concn. (mM)	$i_1$ ( $\mu A$ )	$E_{1/2}$ (V)	$i_1/C$ ( $\mu A/mM$ )
0.0996	4.85	1.009	49
0.299	14.20	1.018	48
0.498	25.2	1.023	51
0.996	48.2	1.009	48

<sup>a</sup> Quoted results are the averages of at least two separate determinations. Potentials are vs. S.C.E.

No oxidation waves were observed for chloride ion in the two sulfate media used.

#### Voltammetry of mixtures of halides

Preliminary studies of equimolar mixtures of iodide and bromide at the 0.2-0.5 mM level in both acidic and neutral solution showed no peak that could be attributed to bromide ion oxidation. However, iodide gave two oxidation waves even in the presence of a hundred-fold excess of bromide. The waves were closer together than in the absence of bromide and occurred in both acidic and neutral K<sub>2</sub>SO<sub>4</sub> background at about  $E_{1/2}$ -values of 0.53 and 0.69 V. With increasing iodide concentration the waves separated somewhat, e.g., 0.01 mM iodide in the presence of 0.1 mM bromide gave  $E_{1/2}$ -values of 0.56 and 0.68 V in both backgrounds whereas 1.0 mM iodide in the presence of 3.0 mM bromide gave  $E_{1/2}$ -values of 0.49 and 0.77 V. Similar effects were noted in the voltammetric determination of iodide in the presence of excesses of bromide and chloride.

Typical results for the determination of iodide in the presence of bromide and of both bromide and chloride are presented in Tables 3 and 4. In order to obtain the

TABLE 3  
VOLTAMMETRIC DETERMINATION OF IODIDE IN PRESENCE OF BROMIDE IN SULFATE MEDIA AT THE R.P.G. ELECTRODE

KI concn. (mM)	KBr concn. (mM)	Current for wave <sup>a</sup>		Iodide concn. calc. <sup>b</sup> on basis of wave					
		I + II		I		I		I + II	
		Range ( $\mu$ A)	Average ( $\mu$ A)	Range ( $\mu$ A)	Average ( $\mu$ A)	Range (mM)	Average (mM)	Range (mM)	Average (mM)
0.5 M K <sub>2</sub> SO <sub>4</sub>									
0.01002	1.003	0.62-0.66	0.64	0.92-1.03	0.97	0.0090-0.0097	0.0094	0.0057-0.007	0.00635
0.03006	1.003	1.68-1.80	1.74	2.25-2.73	2.49	0.00284-0.0305	0.0295	0.0210-0.0267	0.0239
0.03006	3.022	1.23-1.92	1.58	2.07-3.03	2.55	0.0200-0.0327	0.0264	0.0200-0.0305	0.0250
0.1002	3.022	5.33-5.33	5.33	7.43-7.50	7.47	0.0956	0.0956	0.0815-0.0825	0.0820
1.002	3.022	48.5-49.0	48.75	81.5-85.5	83.50	0.977-0.986	0.982	0.920-0.905	0.943
0.5 M K <sub>2</sub> SO <sub>4</sub> + 0.5 M H <sub>2</sub> SO <sub>4</sub> <sup>c</sup>									
0.01002	1.003	0.43-0.59	0.51	0.62-0.81	0.72	0.0080-0.0114	0.0097	0.990-1.020 <sup>d</sup>	1.005
0.03006	1.003	1.62-1.68	1.65	2.10-2.15	2.13	0.0328-0.0340	0.0334		
0.03006	3.022	1.59-1.62	1.60	1.86-1.95	1.91	0.0325-0.0328	0.0327		
0.1002	3.022	4.98-5.36	5.17	6.16-6.74	6.45	0.1000-0.1050	0.1025		
1.002	3.022	48.2-48.8	48.5	77.0-79.4	78.2	0.988-1.000	0.994		

<sup>a</sup> At least two determinations were carried out in each case.

<sup>b</sup> Calibration waves prepared from data summarized in Table I.

<sup>c</sup> Although a second wave appeared in each case in the presence of bromide, no wave appeared for iodide alone; therefore, a calibration wave could not be prepared.

<sup>d</sup> Estimated from Table I data.

TABLE 4

VOLTAMMETRIC DETERMINATION OF IODIDE IN THE PRESENCE OF BROMIDE AND CHLORIDE IN 0.5 M K<sub>2</sub>SO<sub>4</sub>-0.5 M H<sub>2</sub>SO<sub>4</sub> BACKGROUND

KI concn. (mM)	KBr concn. (mM)	KCl concn. (mM)	Wave I current <sup>a</sup>		Iodide found <sup>b</sup>	
			Range ( $\mu$ A)	Average ( $\mu$ A)	Range (mM)	Average (mM)
0.01002	1.002	0.994	c			
0.03006	3.027	2.97	1.80-1.88	1.83	0.0365-0.0385	0.0372
0.1002	3.027	2.97	5.25-5.48	5.33	0.1050-0.1100	0.1067
1.002	3.027	2.97	47.3-48.8	48.0	0.970-1.000	0.984

<sup>a</sup> At least three determinations were carried out in each case.<sup>b</sup> Based on calibration curves prepared from data summarized in Table 1.<sup>c</sup> A wave could not be observed at  $E_{\frac{1}{2}}$  of 0.53 V, although a composite wave was produced

greatest precision it is generally necessary to subtract the background voltammogram from the test voltammogram, *e.g.*, on a point-by-point basis. Determinations based on the first iodide oxidation wave gave the most accurate results in both acidic and neutral solution.

Because iodide alone at very low concentrations often gave no second wave in acidic K<sub>2</sub>SO<sub>4</sub> background, it was not possible to prepare a suitable calibration curve for the determination of iodide in bromide or bromide-chloride mixtures utilizing the total wave height of iodide waves I and II. However, it is possible that an empirical calibration curve could be prepared from synthetic iodide-bromide-chloride mixtures.

Large excesses of chloride did not interfere in the determination of bromide; typical results are shown in Table 5.

TABLE 5

VOLTAMMETRIC DETERMINATION OF BROMIDE IN THE PRESENCE OF CHLORIDE IN 0.5 M K<sub>2</sub>SO<sub>4</sub>-0.5 M H<sub>2</sub>SO<sub>4</sub> BACKGROUND

KBr concn. (mM)	KCl concn. (mM)	Wave current <sup>a</sup>		Bromide found <sup>b</sup>	
		Range ( $\mu$ A)	Average ( $\mu$ A)	Range (mM)	Average (mM)
0.0996	9.98	4.00-4.95	4.48	0.080-0.10	0.090
0.299	9.98	1.45-1.49	1.47	0.295-0.306	0.301
0.498	9.98	2.43-2.45	2.44	0.500-0.500	0.500
0.996	9.98	4.04-4.10	4.07	1.055-1.075	1.065

<sup>a</sup> At least two determinations were carried out in each case.<sup>b</sup> Based on calibration curves prepared from data summarized in Table 2.

### Analytical evaluation

Iodide can be determined down to a lower limit of 0.01 mM by utilizing the first voltammetric wave produced by oxidation of iodide at the R.P.G. electrode. The accuracy over the concentration range 0.01-1.0 mM is about  $\pm 4-5\%$  in acidic potassium sulphate background and somewhat less in neutral K<sub>2</sub>SO<sub>4</sub> background.

Bromide can be determined by an analogous procedure with an accuracy of  $\pm 3-4\%$ .

The calibration wave obtained for iodide alone can be used for determining

iodide in the presence of large excesses of bromide and of bromide plus chloride, the most precise results being obtained in acidic K<sub>2</sub>SO<sub>4</sub> background. Similarly, bromide can be determined in the presence of large excesses of chloride.

The work of SMITH AND ELVING<sup>4</sup> indicates that sulphate, fluoride, chlorate, acetate, perchlorate and nitrate should not interfere in the determination of bromide or iodide.

The mechanism of the electro-oxidation of iodide and bromide in aqueous and non-aqueous solution at the pyrolytic graphite electrode is now being investigated.

#### ACKNOWLEDGEMENT

The authors thank the U.S. Atomic Energy Commission and the Horace H. Rackham School of Graduate Studies of The University of Michigan for their support of the work described.

#### SUMMARY

A voltammetric procedure has been developed for the determination of iodide and bromide by oxidation at the rotating pyrolytic graphite electrode (R.P.G. electrode) in sulfate background. The method can be extended to cover the determination of as low an iodide concentration as 0.01 mM in the presence of large excesses of bromide and chloride, and the determination of bromide in concentrations as low as 0.1 mM in the presence of large excesses of chloride.

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