Coulometric Oxidation of Iodine to Iodine(I)-Bromide with Bromine Generated with Iridium Anode in Hydrogen Bromide Solution

SIGNAR SUNDSTRAND

Department of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

Purified iodine has been oxidized to iodine(I)bromide (IBr_2^-) in 4 M HBr medium with constant current coulometry using an iridium anode. With the method described, results may be obtained with an uncertainty not exceeding 0.01 %. In the coulometric titrations the current density was varied between 3 and 40 mA/cm^2, and the sample of iodine between 0.3 and 4 meq. Gran's method was used to evaluate the equivalence points. Their uncertainties were estimated by a method based on the concept of redox buffer capacity. By conventional analysis, using platinum electrodes in hydrogen chloride or hydrogen bromide media, serious errors arise, mainly due to the dissolution of platinum. A convenient method has been developed to prepare pure hydrogen bromide solutions.

In the preceding communication[1] a simple method was reported for the preparation of pure iodine and several test reactions were given to find its trace contamination level.

We intend to use this material primarily for the study of various equilibria but we also desire to explore its suitability as a universal analytical standard because of its uniquely favourable characteristics.

Iodine is a monoisotopic element, non-hygroscopic and perfectly stable in air. Moreover, it may easily take up or donate electrons.

In the present article we studied iodine as a reducing agent by oxidizing it coulometrically. This approach was chosen to avoid the almost insurmountable difficulties to find a chemical oxidant of a purity comparable with our iodine.

Constant current coulometry combined with potentiometric determination of the equivalence point has proved to be quite easy to adapt for (computerized) automatic operation. Hence whatever degree of accuracy is required, the present analysis can be carried out conveniently in any laboratory with readily available instruments.

METHOD OF ANALYSIS

Introduction. In the present work we have been mainly concerned with the problem of oxidizing iodine to the oxidation state one in the ionic medium 4 M HBr.

Several authors have found that iodine is complexed by bromide and Lang[2] established in 1936 that the I(I) cation binds at most two Br^- ions. Forbes and Faull[3] made the first electrometric investigations of this titration method. Bromine as a coulometric intermediate was first systematically studied by Swift[4] and his co-workers.

Evidence will be presented that bromide can be anodically oxidized to tribromide with theoretical current efficiency under the conditions used in this study.

Thus the titration reaction may concisely be expressed as

$$I_2Br^- + Br_3^- \rightarrow 2 IBr_2^- \tag{1}$$

The proposed procedure contains the following steps: (1) *in situ* purification (pretreatment) of the ionic medium, (2) the start titration, (3) addition of the accurately weighed iodine sample, (4) the main and (5) the end titration.

The cell and the emf measurements. The emf measurements were carried out in a cell without liquid junction:

– Glass electrode | TS | Ir +   (I)
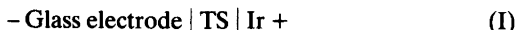
The test solution, TS, consisted at the beginning of the experiment of 120 ml 4M HBr plus a small amount of iodine. After a start titration 0.3–4 meq. of iodine were introduced from an alkaline iodine stock solution, and the main titration was undertaken.

The emf of cell (I) can beyond the equivalence point be expressed as

$$E = E_o(I) + g/2 \lg [Br_3^-]/[Br^-]^3 - g \lg h \qquad (2)$$

In eqn. (2) g denotes $RT\ln10/F$, $E_o(I)$ represents the sum of the concentration independent terms and h is a symbol for the hydrogen ion concentration.

During the coulometric titration the $[Br_3^-]$ never exceeds 0.5 mM and the changes of h and $[Br^-]$ may be considered as negligible. The volume of the test solution may also be regarded as constant. Eqn. (2) can thus be simplified to

$$E = E_o + g/2 \lg (w - w_o) \qquad (3)$$

where E_o is a conditional constant, w is the amount of electrons withdrawn from the solution ($F=96486.7$ As mol^{-1} [5,6]), ensuing the pretreatment, and w_o is the intercept on the w-axis in the Gran plot (*cf.* Fig. 1).

The coulometric circuit. We have used the following electrolysis circuit:

Ir | TS | Cathode compartment   (II)
└ + Constant current source – ┘
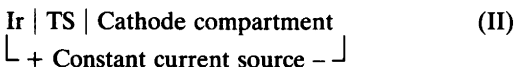
The cathode compartment was a Wilhelm bridge with the following composition:

| 4M HBr | 4M HBr | Hg$_2$Br$_2$ (*s*) | Hg   (III)

As it is seen, the same ionic medium is used throughout the whole cell.

A simplification arises from the high solubility of iodine in 4M HBr. On the basis of the data gathered by Linke[7], the solubility is probably higher than 80 mM, compared with about 1 mM in water, and most titrations could therefore be done in a homogeneous solution. The concentration level 4M has been chosen as a compromise between our desire to keep the impurity concentration as low as possible but to avoid the risk for coulometric side reactions.

ON THE DETERMINATION OF EQUIVALENCE POINT IN REDOX TITRATIONS

General. We used Gran's method[8] for the localisation of the equivalence point. If the following conditions are fulfilled, a plot of the concentration quotient between the electrode-active species *versus* the amount of reagent added yields a *straight line.*

(1) Redox equilibrium is established.
(2) A single electrode reaction occurs.
(3) Sufficient excess of the reagent must have been introduced that its equilibrium concentration may be set equal to its stoichiometric concentration.

As a consequence of these requirements only data obtained at a *certain distance* from the equivalence point can be approximated by a straight line.

The great advantage of Gran's method is that *unsuspected* systematic errors can be detected as a deviation from the theoretical straight line. The other advantage is that only data on one side of the equivalence point are needed. In our case we have not been able to obtain a straight line on the iodine side due to the sluggish attainment of equilibrium.

Error calculus. Differentiation of eqn. (3) gives

$$dw_o = dw - (w - w_o) 2F/RT \, dE \qquad (4)$$

It is to be observed that in this equation E_o is assumed to be an unknown parameter which has to be determined from the same data as w_o. The second term of eqn. (4) for dw_o is proportional to the distance from the equivalence point, so every effort should be made to prepare pure reagents to enable the analyst to carry out reliable measurements with small excesses of the reagent. When the number of measurements is great and the measured quantities are not correlated, the expression for the standard deviation takes the form:

$$\Delta w_o^2 = \Delta w^2 + \{(2F/RT)^2 \Sigma(w_i - w_o)^2 \, dE_i^2\}/(N-2) \qquad (5)$$

where N denotes the number of points distinguished by the subscript i. In deriving this equation it was assumed that the same weight is ascribed to each point.

The concept *redox buffer capacity* β is introduced at this stage to make the discussion more general:

$$\beta = \left(\frac{\partial [ox]/c}{\partial E} \right)_c = - \left(\frac{\partial [red]/c}{\partial E} \right)_c \qquad (6)$$

where the total reagent concentration $C=[ox]+[red]=[Br]_{tot}=[Br^-]+3[Br_3^-]$ is regarded as constant, the derivatives are therefore partial. In our case $[Br_3^-]$ is small compared to $[Br^-]$ and the buffer capacity becomes according to eqns. (2) and (6)

$$\beta=F/RT\,[Br(0)]/[Br]_{tot} \qquad (7)$$

This expression can be introduced into the eqns. (4) and (5):

$$\Delta w_o=\{\Delta w^2+(2V\,[Br]_{tot})^2\,\Sigma(\beta_i dE_i)^2/(N-2)\}^{1/2} \quad (8)$$

Here V is the initial volume of the test solution. Hence the second term of (8) is proportional to the product of the buffer capacity and the precision of the emf measurement, corresponding to the fact that the titration error is proportional to the uncertainty in $[Br_3^-]$, $\Delta[Br_3^-]$, which is obtained when eqn. (6) is integrated. The first term originates from the coulometric equipment.

As we must carry out difference titrations, two error estimates must be made, one for the start and one for the end titration. The two independent errors must be combined to obtain the total error

$$\Delta w_o\,(total)=\{\Delta w_o^2(start)+\Delta w_o^2(end)\}^{1/2} \qquad (9)$$

This equation, divided by the amount of the substance titrated, gives the probable relative error.

The definition of the equivalence point and its evaluation. We estimate the two equivalence points corresponding to the start and end titration with linear regression calculation of the two Gran diagrams (*cf.* Fig. 1). In these calculations we only used $E(w)$ data falling within the *same redox buffer capacity range*. A value for w_o which gives no systematic trend in E_o was calculated with a computer in both titrations. The equivalence point is *defined* classically so that it is
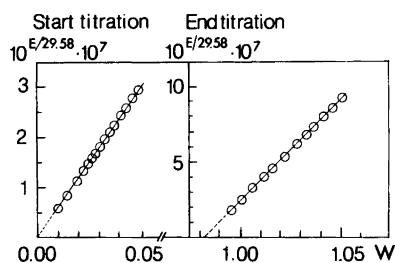

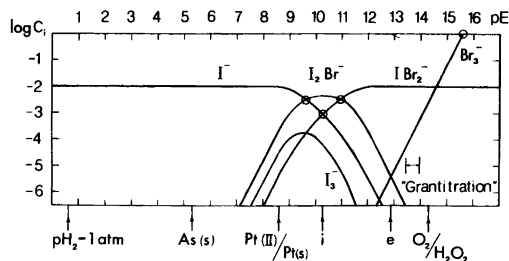Fig. 1. The graphical estimates of the equivalence points for typical start and end titrations.

Fig. 2. The logarithmic concentration of the reacting species as a function of the redox potential. "i" is the iodine point (corresponding to an iodine solution in 4M HBr) and "e" the equivalence point. Circles denote experimental data.

attained when the amount of reagent equals the amount of substance to be determined multiplied by the stoichiometric factor. Thus it is the point where the amount of electrons withdrawn anodically becomes equal to the amount of iodine introduced.

The reagent excess, the concentration of tribromide, was measured with emf, and the point of zero excess, equalling the equivalence point, could be calculated by backward extrapolation. This implies the condition that the *electron deficiency* over Br^- and IBr_2^- is zero at the equivalence point.

The electron deficiency η will take the form

$$\eta/2=[Br_3^-]-[I^-]-[I_2Br^-]-[I_2]-2[I_3^-] \qquad (10)$$

The point where $\eta=0$ is easily recognized in the distribution diagram (Fig. 2) where it is denoted with "e". The electron deficiency condition establishes a relationship between the titration points and the equilibrium concentrations.

It would have been very difficult to attain the same degree of precision if the analyses were not made as difference titrations which virtually eliminate the systematic errors, including the small emf drifts. A typical titration is illustrated in Table 1. The slight difference between E and E_{calc} (with the given w_o and E_o) demonstrates the precision attainable with coulometric titration.

RESULTS

The final series of titrations are summarized in Table 2. The amount of iodine was varied between 0.3 and 4 meq. Two different iodine preparations were used. With the equipment at

Table 1. A typical end titration involving bromine generation.[a]

Point	Real Time	w/mmol electrons withdrawn anodically	E/mV	E_{calc}/mV	β/mV^{-1} 10^6	$10^{2E/g}$ 10^{-7}
18	11.12	0.99515	215.05			
18	12.12		214.95	214.95	1.2	1.8481
19	12.18	1.00040	219.19	219.19	1.7	2.5708
20	12.24	1.00496	221.99$_5$	221.99	2.2	3.1982
21	12.30	1.01091	224.92	224.92	2.7	4.0159
22	12.35	1.01546	226.78	226.78	3.1	4.6416
23	12.41	1.02142	228.86$_5$	228.87	3.7	5.4595
24	12.47	1.02457	229.85	229.85	4.0	5.8946
25	12.52	1.02773	230.76	230.77	4.3	6.3273
26	12.57	1.03158	231.80	231.80	4.6	6.8608
27	13.03	1.03544	232.75	232.76	5.0	7.3874
28	13.08	1.03999	233.81	233.80	5.4	8.0228
29	13.14	1.04455	234.76$_5$	234.77	5.8	8.6420
30	13.19	1.04981	235.80	235.80	6.3	9.3670
	13.27		235.78			
	07.29 [b]		235.50 [b]			

[a] The current was maintained at the 5.0019$_5$ mA level. From eqn. (3) E_{calc} was obtained with w_o=0.98172 mmol and E_o=359.06 mV. The buffer capacity $\beta = F/RT$ [Br(0)]/[Br]$_{tot}$ [b] *Cf.* Fig. 3 illustrating a similar drift.

Table 2. Results. Titration reaction $I_2Br^- + Br_3^- \rightarrow 2IBr_2^-$.

No.	μeq. of iodine introduced	current/mA Titration start-and end	main	yield/%	iodine preparation No.	HBr[a] preparation No.
1	1063	5	20	100.02	1	1
2	980	5	20	100.00	1	1
3	1062	5	20	99.99	1	1
4	311	5	5	100.01	2	1
5	328	10	10	99.99	2	2
6	1178	10	40	99.99	2	2
7	1114	10	40	100.00	2	2
8	4029	10	40	100.00	2	2
9	3934	3	40	100.00	2	2

[a] HBr preparation 1 is prepared from KBr and HClO$_4$, and 2 is commercial HBr purified with Pd(H$_2$).
Note: the amount of iodine is varied by a factor 12, the current density with a factor 8.

our disposal the amount of iodine cannot much exceed 4 meq. Larger samples would require longer electrolysis times and higher currents, while substantially smaller amounts than 0.3 meq. would give larger weighing errors.

It is also shown in Table 2 that two different preparations of the ionic medium, HBr, were used for the analyses. The electrolysis current was made to vary between 5 and 40 mA.

The fact that the results show no systematic variation with current indicates that the current efficiency of tribromide and iodinedibromide

generation exceeds 99.99 %. Another evidence for this statement is given in the experimental part.

Finally we may conclude that the uncertainty of the method described does not exceed 10^{-4}. The standard deviation of the equivalence point determination of the titration illustrated in Table 1 is calculated with eqn. (8) to equal 2×10^{-8} eq. and the total precision can be estimated to 3×10^{-5} according to eqn. (9). Thus the precision in the equivalence point determination is of the same magnitude as the precision of the weighing. Presumably the remaining part of the titration uncertainty is due to systematic errors arising from unidentified side reactions.

EXPERIMENTAL

Titration vessel and electrodes. The titrations have been carried out in a 200 ml vessel provided with six long necks. In contrast to greased surfaces, the teflon coated magnetic stirrer did not react with iodine. Probably its surface contaminants were removed by the pretreatment. The junction between the test solution and the cathode compartment was established with a capillary.

Throughout the titration the test solution was protected from the atmosphere by nitrogen of a slight overpressure provided from a simple manostat. The nitrogen was purified from dust and droplets with a sintered glass filter of porosity G3.

The iridium electrodes were prepared from an iridium foil of 99.9 % purity delivered from the Degussa Company, Germany. The foil was point-welded to a short piece of platinum wire sealed into a soft glass tube provided with a ground joint.

The electrodes were always kept in an oxidizing tribromide/bromide solution, and they were never subjected to ignition, which was found to have a detrimental effect because of the formation of iridium oxide.[9]
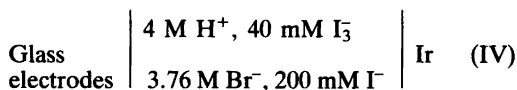
The mercury(I)bromide phase in the *cathode compartment, cf.* cell (III), was prepared *in situ* by anodic oxidation from a mercury pool. During the oxidation the pool has to be vigorously agitated, otherwise a tight mercury(I)bromide crust is formed, and gas evolution occurs. This cell could be used as cathode up to at least 40 mA without any hydrogen evolution.

Some $HgBr_4^{2-}$ is formed in the cathode compartment because of the disproportionation of Hg_2Br_2. However, no complication has arisen

thereby as the bridge was flushed between the experiments. We had difficulties with commercial Hg_2Br_2, which should be tested before use for Hg(II) content and nitrate.

We decided to use a *glass electrode* as an internal reference in this work in order to avoid liquid junctions. Jena H 268 glass electrodes were employed because of their stability.

The long time stability of the glass electrodes was controlled with the following cell:

$$\text{Glass electrodes} \left| \begin{array}{c} 4 \text{ M H}^+, 40 \text{ mM I}_3^- \\ \hline 3.76 \text{ M Br}^-, 200 \text{ mM I}^- \end{array} \right| \text{Ir} \quad \text{(IV)}$$

The emf's of two glass electrodes were measured for ten days. Their difference as well as the emf of cell (IV) was found to change less than 0.15 mV/d which is quite negligible compared to other sources of error.

In this laboratory we have often compared glass and hydrogen electrodes in acid solutions containing up to 5 M HCl or 5 M $HClO_4$.[10] Introducing a correction for the water vapour pressure, the difference between the two electrodes at 1 atm was always found to remain constant within 0.1 mV or better. Hence the glass electrode may be considered to be equivalent with the reversible hydrogen halfcell. The present study indicates that the glass electrode is also useful in 4 M HBr.

Instruments and temperature control. The following equipment was used in the present work: a digital voltmeter, two timers, a constant current source, electrometer amplifiers and a programmable relay scanner. The instruments were controlled by a desktop computer. The instruments used were *calibrated* twice during this work.

The *digital voltmeter* of type HP 2401C from Hewlett-Packard Company was calibrated with a transportable Fluke type 731B DC standard maintained by *Statens Provningsanstalt* (The Swedish Official Standards Laboratory). The voltmeter was set to measure with a precision of 0.01 mV. The noise level amounted however to about 0.03 mV. This could be reduced to 0.01 mV by programming the computer to carry out a smoothing procedure for seven successive emf measurements.

The emf measurements including a glass electrode have been carried out with an Analog Devices *311K electrometer amplifier* assembled in this laboratory. This instrument has been found to have a long time drift smaller than 0.01 mV/week.

To measure the electrolysis time, we used two parallel digital quartz *timers*: type HP 5326B

from the Hewlett-Packard Company and type 5500B from the Ballantine Company. Their quartz frequencies were found to agree within 2×10^{-6}. The timers were triggered by a common signal. The two time period readings always agreed within 0.01 s, corresponding to the time needed to get final relay closures. The *constant current source* was of the type 9770-B from Guildline Instruments Ltd, Canada. The current level fluctuations were kept at about 10^{-5}. To avoid transient signals, the current was passing a dummy resistor of the same magnitude as the electrolysis cell between the titration steps.

The current was determined via the potential drop over a calibrated standard resistor. We had at our disposal a newly calibrated 10Ω resistor (Leeds and Northrup type 4025B). Its uncertainty was 10^{-5} according to the manufacturer. The other resistors used were compared with this standard. The recorded current values are believed to be reliable to within 3×10^{-5}.

The air in the laboratory was controlled and kept constant at 25.0 ± 0.2 °C in the neighbourhood of the instruments. The titrations were carried out in a well guarded silicone oil bath kept at 25.00 ± 0.01 °C.

Procedures. The coulometric titration. Step 1. The experiment commences with a *pretreatment.* The titration vessel is filled with 120 ml of the ionic medium (4M HBr), and a few drops of iodine solution is added. The reducing impurities introduced with the hydrogen bromide, or present on the surfaces of the apparatus, are now assumed to react with the iodine. Next, the excess iodine is completely oxidized to IBr_2^-, then a small excess of bromine is generated (about 10 μeq.). The solution is left overnight, to allow time for sluggish redox reactions to proceed, and the emf is recorded (see Fig. 3).
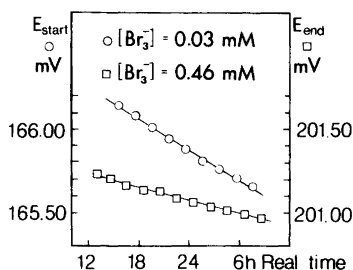

Fig. 3. E, the emf of the cell Glass electrode | TS | Ir+, as a function of time for the starting point (circles) and the last point (squares) of an iodine titration. The slope of the upper line is -0.03 mV/h and that of the lower line -0.015 mV/h. Note the difference in buffer capacity.

Step 2. Overnight some bromine might react, and a coulometric *start titration* must be carried out to get a precise determination of its excess.

By stepwise anodic oxidation of about 100 μeq. of bromine are generated, and the emf is measured at each step. The values $10^{2E/g}$ are plotted versus w in a Gran diagram (see Fig. 1).

Step 3. At this stage the *iodine sample* is introduced into the test solution. This manipulation takes about 30 s and about 10 ml of nitrogen may be estimated to be displaced from the vessel. With a partial pressure not exceeding 10^{-5} atm, the loss of bromine that might occur is certainly less than 0.01 μeq. which is quite negligible.

Step 4. Now the *main electrolysis* starts. It lasts for one to three hours. During this time the current is controlled about ten times every minute and its mean value is successively calculated and stored in the computer. The current is stopped when a small excess of bromine (about 10 μeq) has been generated, and any iodine that diffused into the Wilhelm bridge is reintroduced by flushing into the vessel.

The stability of the emf at this point is controlled (see Fig. 4). At this stage the buffer capacity of the solution is very small, and the absence of any drift or other irregularities provides a severe test for the precision of our experimental approach.

Step 5. Finally the *end titration* is carried out in order to determine the excess bromine just generated (cf. Fig. 1). As far as we could notice, air had no influence on our results and no special care is needed to exclude it. To minimize vapour losses, the vessel is kept closed, and ground glass joints and stoppers are used throughout. To allow for the volume changes during the electrolysis and the flushings, a constant pressure of nitrogen is maintained by a simple manostat.

Further experimental details. In order to obtain results of the highest precision it is necessary to flush the capillary prior both to the start and the end titration in order to reintroduce tribromide. In addition, the volume introduced at the flushing before the end titration must be known,
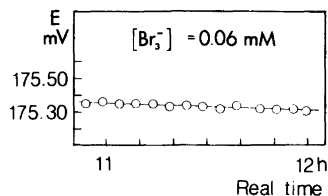

Fig. 4. The drift of E, Glass electrode | TS | Ir+, in the immediate vicinity of the equivalence point. The slope of the line is -0.035 mV/h.

and the result corrected for the amount of impurities introduced thereby. A typical correction for a 1 ml flushing was 0.1 μeq. Within the course of a titration some drops unavoidably gather on the walls of the vessel, and they have to be reintroduced into the solution by shaking the vessel prior to the start and end titrations. This step was rather inconvenient but absolutely necessary.

After each passage of current the potential of the anode was measured, but within a few seconds it deviated less than 0.01 mV from that of the indicator electrode. Thus the current yield for bromine generation must be very near to the theoretical value.

Preparation of pure HBr solutions. Two different methods to prepare pure HBr were developed, and the ionic media made from these preparations are denoted as (1) and (2) in Table 2. With commercial products of *pro analysi* quality no reproducible results could be obtained.

Starting from KBr and HClO$_4$. Potassium bromide of *pro analysi* quality was dissolved at 50 °C in doubly distilled water to give an approximately 6 M solution. Solid impurities were removed by filtration. Next concentrated, iron free, perchloric acid and potassium bromide solutions were added alternately in small portions to a beaker equipped with an effective stirrer, and thus microcrystalline $KClO_4(s)$ formed.

The mixture was chilled to 0 °C with ice, and then small portions of the KBr solution was introduced until no more KClO$_4$ precipitated. The mixture was decanted and filtered and the clear solution was distilled twice. At the first distillation the fraction boiling above 110 °C was collected. This fraction was colored by bromine formed at the elevated temperature over the saturated KBr solution resulting from the distillation.

At the second distillation, water and bromine distilled first and the fraction boiling above 120 °C was collected. The main part was azeotropic acid boiling at 126 °C. The distillation was stopped when the temperature above the residual solution reached 160 °C which is far below the boiling point of perchloric acid (200 °C). Some decomposition to bromine was evident at temperatures higher than 126 °C.

This preparation was found by coulometric titration to contain *oxidizing* impurities amounting to as much as 3 μeq./mol of bromide. No traces of perchlorate could be detected with tetraphenyl arsonium chloride reagent. With spectrophotometry (around 250 nm) the iodine content in this preparation could be estimated to about 1 μeq./mol HBr.

The stock solution was only slightly colored and it was kept under nitrogen and protected from light. Still after one year the coloration was only faint.

The components of the solid KClO$_4$ can be recovered (in a less pure state) by suspending the salt in water with ion exchange resin saturated with hydrogen ion and warming.

Starting from commercial HBr. When the starting material is low in bromine the following procedure may be employed. Concentrated azeotropic, 8M, HBr solution is diluted with the same volume of doubly distilled water. A large platinum net, bearing cathodically precipitated palladium saturated with hydrogen, is inserted into the acid, and hydrogen gas is passed through the solution. This procedure gives within a few hours a colorless product.

When the bromine concentration is high, the palladium may be dissolved and the solution becomes red.

The (Pd-free) colorless solution is finally distilled twice. This preparation was found to contain (colorless) *reducing* impurities amounting to as much as 18 μeq./mol HBr. The advantage of this procedure is that no foreign substances are introduced, and any HAsO$_2$ and arsenious bromide complexes get reduced to arsenic metal. The remaining impurity content is however higher than in the acid made from KBr.

Weighing of the samples. As described in a previous communication[1] iodine was dissolved in sodium hydroxide (Merck "Suprapur") to give iodine stock solutions with concentrations ranging from 0.1 to 0.3 M. This sodium hydroxide preparation was found to contain oxidizing impurities up to 15 μeq./mol. In order to minimize the time of contact with stopcock grease, the desired amount of solution was introduced into a weighing burette of conventional design just before weighing. Another burette type constructed to avoid this source of error is illustrated in Fig. 5.

The iodine solution was transferred from the burette into a vial (0.1 mm×10 mm×90 mm) which was introduced into the cell vessel. With this technique we could avoid removing the burette from the thermostated balance room, shorten the total weighing time and thus increase the precision of the weighing. We varied the weighings between 2 and 7 g of solution using a single pan Sartorius balance readable to 0.01 mg. We estimate the precision of the weighing to 0.1 mg, which was quite sufficient for our purposes. We made a correction for the buoyancy of air in the conventional way. The vial was placed in the cell vessel with the help of tweezers, and was then crushed with a glass rod provided with a ground
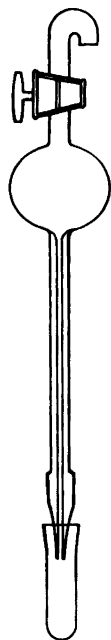
Fig. 5. Weighing burette designed to avoid contact with stopcock grease. The solution is drawn up to the bulb by exhaustion.

glass joint. In order to avoid the formation of a dead space, any remaining large pieces were pulverized at the equivalence point, where the iodine and bromine pressures have their minima. In order to remove impurities, the vials were soaked in a hot strong alkaline solution and then boiled with *aqua regia* before use. This purification was quite necessary to get stable emf readings.

Exploratory experiments in HCl and HBr media. In the initial phase of this investigation, a comprehensive set of iodine oxidations experiments were conducted in hydrogen chloride solutions, where ICl_2^- is formed. This often recommended classical method has proved to provide irregular results (± 1 %). Only platinum could be employed as anode material in this medium. The overpotential for the formation of oxygen on iridium was found to be so low that the amount of chlorine generated was far below the theoretical yield. Graphite anodes absorb considerable quantities of halogens which cannot be regained.

In another series of experiments we used platinum electrodes in HBr media. Also in this case we found both positive and negative errors (± 0.15 %).

Our test solutions were found to contain an appreciable amount of platinum ions which could be detected by cathodic deposition on a bright platinum foil. Deposition could be observed when platinum had been used as anode in a pure hydrogen bromide solution. An attempt was made to estimate the amount of dissolved platinum with atomic absorption spectroscopy. But as the amounts are close to the detection limits of this method, the results may be regarded as semiquantitative only. We found in three test solutions 0.3, 0.4, and 0.6 μmol of Pt. This was about the magnitude expected on the basis of the spread of the results of the coulometric titrations. The dissolution of traces of platinum was also visible on photomicrographs made prior to and after a bright platinum foil has been used an anode.

Thus dissolution of platinum causes considerable systematic errors also at the low redox potentials (600–850 mV) met in our titrations, a fact that seems not to have been reported earlier.

CONCLUSIONS

Within the frame of the present project the following criteria have proved to be indispensable in order to perform coulometric redox titrations of the highest accuracy.

(1) Use of inert electrode materials like iridium.

(2) Strict difference titration involving *in situ* purification ("pretreatment").

(3) Evaluation of the equivalence point with rigorous error estimate based on reversible potentials transformed to a Gran plot.

(4) Insensitivness to oxygen, like the redox couple IBr_2^-/I_2Br^-.

(5) The redox potentials must throughout the electrolysis lie within the limits set by the decomposition potentials of water *e.g.* by choosing a HBr medium.

Further experiments based on these principles, combined with improved instrumentation, may very likely provide results of substantially lower uncertainty and open the way for the re-evaluation of the Faraday constant.

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