

# Coulometric Reduction of Iodine with Copper(I) in Sodium Chloride–Mercuric Chloride Media with Iridium Cathode

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Purified iodine has been reduced to iodide with copper(I) ions generated by constant current coulometry on an iridium cathode, using the ionic medium 3 M NaCl, 0.3 M CuCl<sub>2</sub>, 0.05 M HgCl<sub>2</sub>. This solution disproportionates iodine to HgICl<sub>3</sub><sup>2-</sup> and ICl<sub>2</sub><sup>-</sup>. The redox potential is raised thereby into the vicinity of the half-cell potential of the O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> couple (0.7 V).

Gran's method was used to evaluate the potentiometric equivalence point.

The uncertainty of our analysis was found to increase from ±0.03 % to 0.10±0.04 % as the iodine sample was raised from 0.2 to 1.2 mmoles because of the oxygen error. Platinum cathodes gave results, which could not be reproduced.

The present communication represents the third part of a series dealing with the preparation and application of purified iodine. The preceding article<sup>1</sup> summarized our comprehensive oxidation experiments.

For practical and theoretical reasons we turned to the far more difficult problem of reducing iodine to iodide by constant current coulometry. Our main intention has been to provide a method for the standardization of reducing agents.

Moreover one should take advantage of the almost unique property of the element iodine: that it can readily accept as well as donate one electron. Hence its purity can be tested in several ways.

There are three principal sources of error in iodometry: oxidation of iodide by oxygen (air) in acid solutions, incomplete attainment of redox equilibrium between iodine and the reagent, and loss of iodine or its reaction products by volatilization. The magnitudes of these errors are

difficult to estimate on the basis of the published literature. The present work aims at throwing some light on these questions.

For obvious reasons an *intermediate* reducing agent is required in constant current coulometry. This must be generated *in situ* from the oxidized form of a species, kept at a high and virtually constant concentration in the course of the titration.

A redox intermediate must satisfy three main requirements. It must be generated with a theoretical current efficiency, the intermediate should react rapidly and stoichiometrically, and finally its excess must be determinable, if possible, by potentiometry.

In Swift's laboratory<sup>2</sup> these questions were studied systematically, and it was found that these three conditions are best met by the Cu(II)–Cu(I) couple in a chloride medium. We have corroborated their conclusion. Several other reducing intermediates have been proposed such as Fe<sup>2+</sup><sup>3,4,5</sup>, Ti(III)<sup>6</sup>, the Fe(II)–EDTA-complex<sup>7</sup>, and Sn(II)<sup>8,9</sup> but they have proved unsuitable for our purpose. Another advantage of the Cu(II)/Cu(I)-couple is that its  $E^{0'}$  is as high as 0.51 V in a 3M NaCl-medium<sup>10</sup>. Thus the redox potential can be kept in the vicinity of the potential of the competing couple O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> (0.7 V) during the whole titration<sup>11</sup>.

## METHOD OF ANALYSIS

*Procedure.* The titration procedure consists of five principal steps: (1) Pretreatment of the ionic medium. (2) Start titration. (3) Main electrolysis, in which an excess of Cu(I) is generated to

shorten the lifetime of  $\text{ICl}_2^-$ . (4) Introduction of the iodine sample. (5) End titration.

*General.* We decided to carry out the coulometric reduction of iodine in a medium consisting of 3 M NaCl, 0.3 M  $\text{CuCl}_2$  and 0.05 M  $\text{HgCl}_2$ . Under these conditions the concentration changes during a titration may be conveniently visualized with the help of Fig. 1 which shows lines for the copper and iodine bearing species:

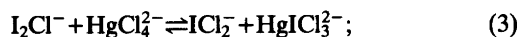
$$\lg [\text{Cu(I)}]/[\text{Cu(II)}]=f(\text{pE}) \quad (1)$$

and

$$\lg C_j/a_i^{1/2}=f(\text{pE}) \quad (2)$$

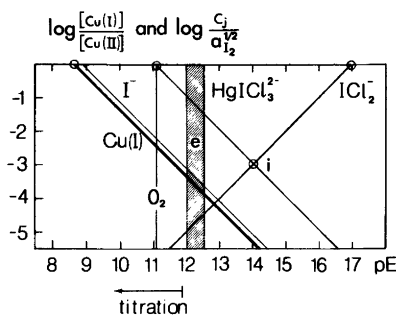
where  $a_i$  denotes the activity of iodine and solid iodine has been taken as reference;  $C_j$  stands for  $[\text{ICl}_2^-]$ ,  $[\text{I}^-]$ , or  $[\text{HgICl}_3^{2-}]$ . The latter ion, which predominates, represents in the following discussion the sum of all the iodide bearing mercury(II) species. The formal potentials needed to construct the redox diagram are denoted by circles. They have been determined from emf measurements, as described in a separate communication<sup>10</sup>.

In our solvent *disproportionation* of iodine occurs:



$$\lg K = -2.0 \quad (4)$$

Thereby pE in an iodine solution is increased to the concentration independent value 14.0, denoted by *i* in the diagram, while in the absence of  $\text{HgCl}_2$  it is as low as 12.8. Another advantage is that the solubility of iodine is increased to

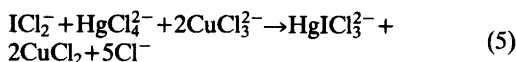


**Fig. 1.** A simplified redox diagram for copper and iodine in the medium 3M NaCl, 0.3M  $\text{CuCl}_2$ , 0.05M  $\text{HgCl}_2$ . Symbols: "i": pE of an  $\text{I}_2$ -solution, "e": zone of equivalence points, line "O<sub>2</sub>": pE( $\text{O}_2/\text{H}_2\text{O}_2$ ) at pH 2.5 and circles: data<sup>10</sup>.

about 4 mM by the addition of 0.05 M mercury(II).

The intermediate Cu(I) was generated from Cu(II), present in a large excess in the solution.

The *titration reaction* can consequently be summarized as:



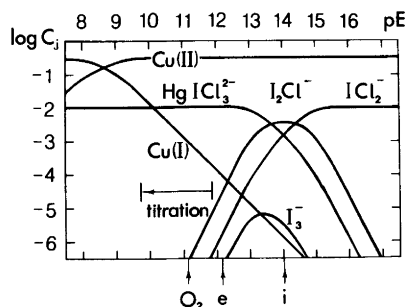
The pH was chosen to lie in the vicinity of 3. This represents a compromise between conflicting demands, and is situated near to the maximum pH at which the reaction between  $\text{IO}_3^-$  and  $\text{I}^-$  is still sufficiently rapid. Iodate ions are introduced into the solution with the alkaline iodine stock solution<sup>1,12</sup>.

The *equivalence point* is denoted by *e* in Figs. 1 and 2. It is the point with zero electron excess over  $[\text{Cu(II)}]$  and  $[\text{I(-I)}]$  and the following equation is valid:

$$[\text{Cu(I)}] = 2([\text{ICl}_2^-] + [\text{I}_2\text{Cl}^-] + [\text{I}_2] + [\text{I}_3^-]) \quad (6)$$

Fig. 2 resembles a conventional pH diagram. It has been constructed because the concentrations of polynuclear species ( $\text{I}_3^-$ ,  $\text{I}_2\text{Cl}^-$  and  $\text{I}_2$ ) cannot be properly illustrated in a relative diagram.

The lines for the three last species in eqn. (6) are omitted from Fig. 1 for the sake of simplicity. They should be represented by two horizontal lines at  $-1.3$  for  $[\text{I}_2\text{Cl}^-]^{1/2}$  respectively  $-1.6$  for  $[\text{I}_2]^{1/2}$ <sup>13</sup>, and the  $[\text{I}_3^-]^{1/3}$ -line with a slope of  $-1/3$  ( $\text{pE}^0 = 8.8$ , estimated with data from<sup>10</sup>).



**Fig. 2.** Logarithmic distribution diagram<sup>10</sup> for the copper- and the iodine bearing species in 3M NaCl medium at the 0.3 M  $[\text{Cu}]_{\text{tot}}$  and the 0.01 M  $[\text{I}]_{\text{tot}}$  levels. Symbols: "i": pE of an  $\text{I}_2$  solution, "e": equivalence point, "O<sub>2</sub>": pE( $\text{O}_2/\text{H}_2\text{O}_2$ )<sup>11,17</sup> at pH 2.5.

The  $pE$  at the equivalence point varied from 12.0 to 12.5 as the amount of iodine was changed systematically in our titrations. In conventional iodine titration, for instance with thiosulfate,  $pE$  at the equivalence point may be estimated to 7.5 (440 mV), which is about 5  $pE$  units (300 mV) lower than our actual values.

**Potentiometry.** We used a cell without liquid junction to measure the Cu(II)/Cu(I) potential in the test solution (TS):

– Glass electrode (GE) | TS | Ir (indicator electrode) + (I)

Here the test solution contains NaCl, CuCl<sub>2</sub>, HgCl<sub>2</sub>, HCl, I<sub>2</sub>, the Cu(I) generated coulometrically as well as the products of the different redox and complex formation reactions. The emf of this cell at 25 °C can be written as

$$E = E(\text{Ir}) - E(\text{GE}) \quad (7)$$

Where

$$E(\text{Ir}) = E^0[\text{Cu(II)/Cu(I)}] + 59.16 \lg [\text{Cu(II)}]/[\text{Cu(I)}] \quad (8)$$

$$E(\text{GE}) = E^0(\text{GE}) + 59.16 \lg h \quad (9)$$

Of these terms the  $E^0$ 's represent isothermal constants and  $h = [\text{H}^+]$ .

As the composition of the test solution changed but slightly in the course of a titration, we could neglect the variation of the activity coefficients of the reacting species.

Therefore the emf of cell (I) can be written in the simple form

$$E = E_0 + 59.16 \lg [\text{Cu(II)}] - 59.16 \lg [\text{Cu(I)}] \quad (10)$$

The [Cu(II)] decreases very little during the start or end titrations, and it may also be regarded as a constant in the first estimate of the equivalence point.

This estimate was then improved by calculating the correct [Cu(II)] in all the measured points.

*The evaluation of the equivalence points and the titration error estimates.* These calculations were carried out according to the same principles as in the oxidimetric titrations<sup>1</sup>. Titration 6 in Table 1 has a precision of about  $2 \times 10^{-5}$ . Thus the titration error, which is fifty times higher in this

case, is certainly not affected to any appreciable extent by the imperfections of the localization of the equivalence point.

## EXPERIMENTAL

**Techniques.** Our choice of experimental conditions has been guided by the desire to minimize the oxygen error. Further we decided for practical reasons to use a technique involving instruments and other equipment readily available in any modern laboratory.

Once the titration had been started, the cell was exposed to the atmosphere no longer than a few minutes altogether. The introduction of redox-active impurities, dust and droplets was avoided by maintaining a slight overpressure of argon. This technique is certainly to be preferred to a continuous stream of gas.

The argon was purified by passing it through a copper column held at 150 °C in order to remove oxygen, and then through a washing bottle containing 3M NaOH. This was saturated with solid Ag<sub>2</sub>O in order to oxidize any traces of reducing impurities like CO or H<sub>2</sub>. Finally the gas passed through two sintered glass filters of porosity G3.

In *model experiments* this purified gas could be passed through solutions with a low redox buffer capacity<sup>1</sup> ( $\beta = 20 \times 10^{-6} \text{ mV}^{-1}$ ) for more than one hour without affecting the redox potential more than 0.01 mV.

For reasons, which we discussed in detail in the previous communication<sup>1</sup>, we used the *ampoule technique* to introduce the iodine sample.

**Titration procedure. Step 1. Pretreatment in situ** purification of the ionic medium to reduce the redox impurity level. Sufficient purified hydrochloric acid was added to completely neutralize the amount of hydroxide ions introduced later with the iodine sample. Immediately before each of the three "Gran titrations" (see below) argon was passed through the solution for about 20 minutes to remove oxygen. About three ml of the ionic medium was transferred by exhaustion up into the capillary of the Wilhelm bridge after the initial treatment with argon. Thereby the capillary could later be flushed with a solution of known composition.

A Gran titration (the very first) was carried out to determine the impurity content of the medium.

After this the solution was left overnight to attain chemical equilibrium and a stable temperature in the cell vessel (*cf.* Fig. 3). In the morning a few drops of iodine solution were added to

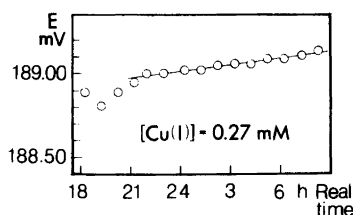


Fig. 3. Drift of the emf of cell (I) preceding a start titration. (The cell was put into the thermostat at 18.00 h). The slope of the line is  $0.01_3$  mV/h.

diminish the Cu(I) concentration.

**Step 2. Start titration.** A Gran titration was now made to determine the excess of Cu(I) and to establish a reference redox potential level defined by eqn. (6).

**Step 3. The main electrolysis.** An excess of about 0.2 mM Cu(I), compared to the amount of iodine introduced in step 4, was generated to shorten the lifetime of  $\text{ICl}_2^-$ . This is the lowest concentration providing reversible redox potentials.

**Step 4. Iodine sample.** During the introduction of the ampoule the neck of the cell was flushed with argon streaming through a glass capillary. No gas was passed through the test solution itself, not to expel any ICl or iodine formed. The establishment of redox equilibrium (5) was controlled (cf. Fig. 4), and it was always found to be attained within 15–20 min.

**Step 5: End titration.** The third Gran titration with stepwise generation of Cu(I) determines the equivalence point. The other details were similar to those described in the previous work.<sup>1</sup>

A complete end titration is shown in Table 2. As is clear from this table a typical end titration

Table 1. Final series of iodometric titrations.

No.	$\mu\text{eq.}$ introduced	Current/mA start- and end-	main titration	Yield / %
1	392	10	10	100.03
2	434	10	51	99.98
3	1069	10	10	99.98
4	2337	10	51	100.05
5	2351	10	10	100.12
6	2356	10	51	100.10 <sup>a</sup>

<sup>a</sup> Medium: 3M NaCl + 0.5M  $\text{CuCl}_2$  + 0.3 M  $\text{HgCl}_2$ .

Note: The amount of iodine is varied with a factor 6, the current with a factor 5.

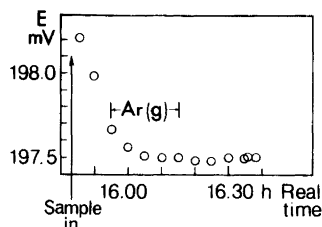


Fig. 4. The emf of cell (I) as a function of time illustrating the rapid attainment of the equilibrium (5), and the purity of our argon. The alkaline iodine sample was introduced at 15.40 h, prior to this instant  $E$  was 65.05 mV.

lasts for about one hour, while a complete experiment takes from three to five hours. The equilibrium is established within one minute ensuing the passage of current, and the potentials have always been found to be very stable.

This conclusion is also evident from Figs. 3, 4 and 5. The potentials of the cathode and the indicator electrode did always agree within 0.01 mV. It is also apparent from Table 2 that most of the data and the calculated emf values also agree to within this limit.

**Preparation of the ionic medium.** For our present purposes only contaminants which may participate in redox reactions have been of interest. Most commercial chemicals, like our starting substance NaCl, contain as the main redox impurities the heavy metal ions  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{VO}_2^+$ , and  $\text{Cr}^{3+}$ . Fortunately these ions form slightly soluble hydroxides, oxides or other basic salts already in acid solutions. They may therefore be conveniently eliminated by coprecipitation for instance with freshly prepared hydrated silica at about pH 6 (cf. Ref. 14). We used instead *in situ* precipitated copper hydroxochloride as the carrier since our medium contained 0.3 M  $\text{CuCl}_2$ . The purified ionic medium has been found, by coulometric titration with Cu(I) ions,

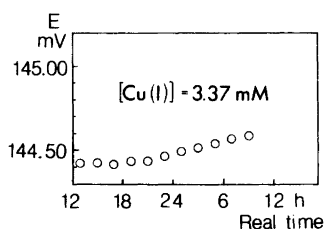


Fig. 5. Stability of the emf of cell (I) after an end titration and the long time drift which is about  $0.01_3$  mV/h at  $t > 20.00$  h.

Table 2. A typical end titration.

Cell: - GE | TS | Ir +

No.	Time/h	$w^a$ /mmol	$E$ /mV	$E_{\text{calc}}^b$ /mV	$\beta/10^6 \text{ mV}^{-1}$
23	11.28	2.38631	203.08	203.12	22
	11.38		203.08		
24	11.41	2.38803	201.57 <sub>5</sub>	201.61	23
25	11.44	2.39203	198.38	198.41	27
26	11.46	2.39603	195.55	195.56	30
27	11.49	2.40004	192.99	192.99	32
28	11.53	2.40519	190.03	190.02	37
29	11.55	2.41147	186.82	186.82	42
30	11.58	2.41661	184.46 <sub>5</sub>	184.46	46
31	12.01	2.42290	181.84 <sub>5</sub>	181.84	51
32	12.04	2.42804	179.89	179.88	55
33	12.08	2.43432	177.68	177.68	59
34	12.11	2.44060	175.64 <sub>5</sub>	175.65	64
35	12.14	2.44688	173.76 <sub>5</sub>	173.76	69
36	12.17	2.45201	172.32	172.32	73
37	12.21	2.45829	170.65	170.66	78
38	12.23	2.46342	169.36 <sub>5</sub>	169.37	82
39	12.26	2.46969	167.87 <sub>5</sub>	167.89	86
40	12.30	2.47597	166.47	166.48	92
	14.48		166.46		

<sup>a</sup>  $w$  is the amount of electrons introduced at the cathode.<sup>1</sup> <sup>b</sup> According to eqn. (10):

$$E_{\text{calc}} = 11.14 + 59.16 \lg \left[ \frac{(50 + 2.35789 - w)}{(w - 2.35789)} \right]$$

Note:  $\beta = F/RT [\text{Cu(I)}]/[\text{Cu}]_{\text{tot}}$  is the redox buffer capacity.<sup>1</sup>

to contain about 120  $\mu\text{eqs./l}$  of a reducing agent. This contamination level turned out to decrease rapidly on standing. In one case, studied in detail, it dropped to 10  $\mu\text{eqs./l}$ . The latter figure corresponds to a contamination ratio of 3 parts per  $10^6$ .

This gradual decrease of the concentration of reducing agent (presumably Cu(I)) stopped after three weeks and it is probably due to the oxidation by air which was let in when a sample was withdrawn for analysis. It should be pointed out that in the course of the pretreatment the impurity concentration was reduced still further.

*The electrolysis cell.* As the electrolysis cell we used a Wilhelm bridge of the general arrangement

(Cathode) Ir | TS | Salt bridge | Anode compartment (II)

The salt bridge had the composition

| Ionic medium | 3M LiCl

and the anode compartment

| saturated LiI | Pt-anode (III)

Lithium chloride and iodide have been preferred because of their high solubilities. The anode was a 2  $\text{cm}^2$  platinum net. During the electrolysis  $\text{I}_3^-$  is formed:



This oxidation could be carried out with the theoretical current efficiency up to at least 51 mA. No evidence has been found for oxygen evolution. This current cannot be much exceeded because of the evolution of hydrogen on the cathode. When this occurs, a large difference between the potentials of the cathode and of the indicator electrode remains after the passage of current.

The ampoules and the instruments used were the same as earlier.<sup>1</sup> A new voltmeter, HP 3456A, (Hewlett-Packard) has been employed for the emf measurements and the coulometry. Thereby the accuracy and the precision of emf readings have been greatly enhanced.

## EXPLORATORY EXPERIMENTS

In the initial phase of this investigation a great number of exploratory experiments were made which might be of some general interest and will therefore be shortly summarized below.

*Comparison of platinum and iridium electrodes.* We could not use platinum electrodes in our 3M NaCl medium. From six titrations with platinum electrodes of about 270 mg iodine (2 mmoles) we found the average yield 100.09  $\pm$  0.24 %, while six titrations with iridium electrodes with the same amount of iodine and under otherwise identical conditions provided 100.09  $\pm$  0.04 %.

*Choice of acidity level.* It was an inconvenience to work in acid solutions (pH 2–3). We found that at pH about 4.5 (acetic acid–acetate buffer) highly stable Cu(II)/Cu(I) potentials can be obtained, however, at this pH the reaction between  $\text{IO}_3^-$  and  $\text{I}^-$  (introduced with the iodine stock solution) to iodine was too slow. In our medium this reaction was sufficiently rapid only at pH < 3.

In some experiments we performed the electrolysis in a neutral solution, acidified just prior to the addition of iodine, waited until equilibrium (5) had been established and then realkalified. This was done by introducing a concentrated sodium acetate solution [purified by precipitating  $\text{Cu}(\text{OH})_2(\text{s})$ ]. However, this technique did not provide the desired result, probably because of small amounts of redox impurities in the acetate solution.

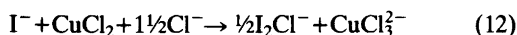
*Choice of intermediate reagent.* In a series of preliminary experiments we attempted to find the most suitable intermediate for high precision coulometric reduction of iodine.

We first tried *Sn(II)* which has proved to be a rapid iodometric reagent in volumetric and in potentiometric titrations. Moreover, the Sn(II)/Sn(IV) couple in hydrochloric acid medium has been found (in our laboratory) to furnish reversible potentials, uninfluenced by the choice of the electrode material (Hg or Pt). However, when iodine was introduced, difficulties arose. The redox potential drifted slowly without showing a tendency to attain a stable value. Moreover, different indicator electrodes in the same solution sometimes differed by many millivolts. These complications are probably due to the slow replacement of chloride by iodide in the chloride

complexes of tin. Similar troubles were met with in bromide medium.

According to Bock and Greiner<sup>15</sup> the following Sn(IV)/Sn(II) formal potentials are valid in 1M acid medium: 147 mV (HCl), 127 mV (HBr) and –38 mV (HI). This illustrates the higher stabilities of the iodide complexes. We next turned to the *ferrous ion*, but neither the fluoride nor the phosphate complex could be employed, because the rate of iodine reduction was very sluggish, and we could not find any intermediate reagent to catalyze the reaction. The Fe(II)-EDTA complex proposed by Stein<sup>7</sup> could not be utilized because of the high pH (pH 6) required.

Finally, we have taken up the study of *cuprous ion* in chloride medium. Normally when iodide and  $\text{CuCl}_2$  are mixed in a chloride medium the following reaction occurs:



But if iodide could be complexed, it would be possible to make this reaction to proceed from right to left.

Furman and Miller<sup>16</sup> found that when Hg(II) is present, the free iodide concentration is diminished so much that iodine can be titrated with reductants whose  $E^0$  values are as high as 0.5–0.6 volt. They also found stable potentials near the equivalence point indicating that the rate of oxidation of complex bound iodide by oxygen is much suppressed. The method presented in this communication is based on this experience.

## RESULTS

The final series of analyses are summarized in Table 1. The amount of iodine sample was varied between 400 and 2000  $\mu\text{eqs.}$ , and the current between 10 and 51 mA. It is apparent from Table 1 that we got a positive error of as much as 0.1 % at the largest amounts of iodine.

This error is probably caused by the residual oxygen, which has thus proved to be significant, even though the overwhelming part of the iodide ions in our experiments was bound in the form of mercuric complexes (*cf.* Ref. 10). Oxygen is known to act as a very slow oxidizing agent at 25 °C, hence the difference between the three first and the three last experiments is most likely due to the prolonged electrolysis period as well as to the lower redox potentials encountered in titrations 4–6.

## CONCLUSIONS

All the problems we met with in this study are presumably due to the residual oxygen remaining after the pretreatment of the test solution.

It is clear from Table 1 that for maximum precision and accuracy small amounts of iodine must be titrated as rapidly as possible without sacrificing the weighing precision, the accuracy of the equivalence point evaluation and the exact determination of the current time integral. The best compromise is probably not far from the conditions chosen in experiments 1 to 3. To raise the precision and accuracy of the coulometric iodine reduction to the vicinity of 0.01 % further efforts are needed to suppress the oxygen error. Preheating the test solution might be one of several possible ways.

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