Investigation is under way to determine whether amounts of iodine greater than 0.005 mg. may be determined colorimetrically by use of the starch–iodide reaction.

Summary

1. The color produced by starch and iodine in the absence of other salts may be used as a colorimetric measurement of the iodine present in amounts ranging from 0.0005 to 0.005 mg. with an accuracy of 0.0001 mg. in the colorimetric reading.

2. The color produced is proportional to the amount of iodine present.

3. The chromogenic substance is stable for at least one hour when compared against a standard made at the same time.

4. Temperature has no effect on the intensity of the color produced up to 70°, after which the color produced is less.

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[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE MEDICAL CLINIC OF THE JOHNS HOPKINS UNIVERSITY]

OXIDATION-REDUCTION POTENTIALS AT CARBON AND TUNGSTEN ELECTRODES

BY LOUIS B. FLEXNER AND E. S. GUZMAN BARRON

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It has been shown[1] that the potentials of cysteine solutions obtained at mercury electrodes are related to mercury-thiol compounds and doubt was cast upon the significance of the potentials obtained at platinum and gold electrodes. It was thought probable that further light would come from investigation of the behavior of cysteine at other electrodes. Of several of these studied, carbon and tungsten appear most promising. This note concerns the behavior of carbon and tungsten electrodes with simple oxidation–reduction systems, the understanding of which must precede investigations on the more complex cysteine systems. Pure graphite was obtained from the Acheson Graphite Company. Tungsten wire came through the courtesy of the General Electrical Company.

The behavior of graphite and tungsten was first studied in two well-poised oxidation–reduction systems of fairly positive E_0. Quinhydrone was first chosen, measurements being made in the presence of air. Table I shows excellent agreements between graphite and gold-plated platinum electrodes in quinhydrone systems in Michaelis' standard acetate buffer, Sørensen's phosphate mixtures, and $N/10$ hydrochloric acid. Purity of carbon is here unimportant, the rods of a carbon arc lamp or the core of a "lead" pencil giving identical results. Tungsten on the other hand gives entirely discrepant values.

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[1] Barron, Flexner and Michaelis, *J. Biol. Chem.*, **81**, 743 (1929).

TABLE I

THE POTENTIALS OF QUINHYDRONE AT GRAPHITE AND GOLD-PLATED PLATINUM ELECTRODES (AGAINST SATURATED CALOMEL ELECTRODE, TEMPERATURE 20°)

Electrode	E. m. f. in volts	Substance
C	+0.38835	N/10 HCl
Au–Pt	+ .3886	
C	+ .18015	Michaelis' standard acetate
Au–Pt	+ .18025	
C	+ .04805	Sørensen's phosphate mixture
Au–Pt	+ .04800	

Reference to Table II gives results typical for a ferro–ferricyanide system in the presence of purified nitrogen. Throughout the titration, the potential at carbon is 1 to 1.5 millivolts more negative than at platinum and gold, whereas tungsten gives values 5 to 10 millivolts more negative than the noble metals. The potential is established with the same rapidity at all these electrodes.

TABLE II

THE POTENTIAL OF A FERRO–FERRICYANIDE SYSTEM AT GOLD-PLATED PLATINUM, PLATINUM, GRAPHITE AND TUNGSTEN ELECTRODES

T, 30°. *M*/1000 $K_4Fe(CN)_6$ in *M*/1 KCl titrated with $K_3Fe(CN)_6$ (*M*/10 in *M*/1 KCl)
E in volts referred to the normal hydrogen electrode

Au	Pt	C	W	*M*/10 $K_3Fe(CN)_6$ added
+0.4117	+0.4114	+0.4037	+0.3684	0.04
.4400	.4398	.4367	.4277	.14
.4524	.4523	.4503	.4397	.21
.4560	.4560	.4540	.4457	.27
.4643	.4641	.4626	.4544	.39
.4730	.4729	.4716	.4642	.51
.4777	.4776	.4763	.4694	.64
.4830	.4830	.4816	.4751	.78
.4891	.4891	.4881	.4820	1.02
.4947	.4947	.4937	.4880	1.23
.4985	.4985	.4975	.4921	1.43
.5043	.5043	.5033	.4982	1.74
.5066	.5066	.5056	.5005	1.84
.5083	.5083	.5075	.5031	2.00
.5112	.5113	.5104	.5056	2.18

The behavior of graphite and tungsten electrodes was then studied in oxidation–reduction systems nearer the cysteine range, and for this purpose indigo disulfonate and methylene blue were used. The results with indigo disulfonate alone will be discussed here—they can be accepted as completely typical of methylene blue. Reference to Table III shows that there is excellent agreement between graphite, gold and platinum electrodes throughout the titration range of the dye. Until the dyestuff system is about 2% reduced, it is necessary to wait approximately one-half hour for the final values at graphite. Thereafter this electrode gives the same sharp, rapidly established potentials as the platinum and gold. Failure to wait for final values at graphite in the early stages of dye reduction produces a discrepancy between its potential and that of platinum which persists until there is approximately 20% dye reduction. This last result is not to be explained by presence of oxygen in the carbon (carbon adsorbs 80% more oxygen than nitrogen), for heating the carbon rod at 400° in a current of purified nitrogen was without benefit. It is noteworthy that graphite rods in these last experiments are easily "poisoned," and often give reliable results in but a single experiment. Crude carbon is unusable.

TABLE III

TITRATION OF INDIGO DISULFONATE WITH $Na_2S_2O_4$

Concentration of dye, *M*/1000 in phosphate buffer (*M*/15 = 30 cc. + 20 cc.) Buffer *P*H, 7.39. *T*, 30°

$Na_2S_2O_4$ added cc.	*Eh* in volts Au plated Pt	Graphite	Diff. between Au and C, volts
0.03	−0.0704	−0.0691	−0.0013
.10	− .0945	− .0935	− .0010
.135	− .1013	− .1007	− .0006
.24	− .1103	− .1101	− .0002
.57	− .1248	− .1244	− .0004
.89	− .1313	− .1314	+ .0001
1.18	− .1372	− .1370	− .0002
1.52	− .1434	− .1432	− .0002
1.83	− .1486	− .1484	− .0002
2.13	− .1563	− .1560	− .0003
2.24	− .1602	− .1600	− .0002
2.34	− .1642	− .1639	− .0003
2.49	− .1742	− .1736	− .0006
2.58	− .1861	− .1854	− .0007
2.61	− .2070	− .1997	− .0073

TABLE IV

TITRATION OF INDIGO DISULFONATE WITH $Na_2S_2O_4$

M/1000 Indigo disulfonate in Sørensen's phosphate buffer (*M*/15 = 30 cc.) 20 cc. of same buffer added. Total, 50 cc. *P*H, 7.39. *T*, 30°

$Na_2S_2O_4$ added cc.	*Eh* in volts Bright Pt	W	Diff. between Pt and W, volts
0.06	−0.0873	−0.0900	+0.0027
.09	− .0925	− .0925	+ .0000
.19	− .1060	− .1050	− .0010
.30	− .1132	− .1110	− .0022
.41	− .1181	− .1173	− .0008
.51	− .1221	− .1211	− .0010
.61	− .1256	− .1249	− .0007
.71	− .1281	− .1270	− .0011
.82	− .1307	− .1299	− .0008
.99	− .1347	− .1337	− .0010
1.21	− .1383	− .1385	+ .0002
1.42	− .1420	− .1417	− .0005
1.53	− .1443	− .1431	− .0012
1.66	− .1472	− .1457	− .0015
1.85	− .1506	− .1492	− .0014
2.03	− .1552	− .1534	− .0018
2.19	− .1590	− .1561	− .0029
2.38	− .1690	− .1645	− .0045
2.48	− .1750	− .1695	− .0055
2.59	− .2071	− .1812	− .0259

Tungsten gives sharp values in these dyestuff systems, but agreement with platinum is not so valuable as with graphite. Values are identical in those ranges where the dye system is particularly well poised, *i. e.*, 30 to 70% reduction, and in isolated instances values may be given agreeing with platinum to within ±2 millivolts from 5 to 95% reduction. Table IV portrays the usual experiment.

Hydrogen gas is without detectable effect on graphite and tungsten electrodes, and in this respect it behaves in a manner similar to mercury electrodes, since there is no measurable difference of potential whether the solution be saturated with nitrogen or hydrogen.

Conclusion

Graphite and tungsten electrodes have been tested in oxidation–reduction systems. In the quinhydrone system graphite gives results identical with those obtained at blank platinum and gold-plated platinum; whereas tungsten gives entirely different values.

In the ferro–ferricyanide system graphite gives measurements one to two millivolts less than platinum; whereas those with tungsten are 5 to 10 millivolts less.

Graphite gives the same results as platinum in a dyestuff system, be it well or poorly poised; whereas tungsten gives reliable results only when the system is well poised.

The potentials of graphite and tungsten against a reversible dye system are unaffected by change from a nitrogen to a hydrogen atmosphere.

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THE PREPARATION OF MANGANESE-FREE MAGNESIUM

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In the course of an investigation of the possible function of manganese in animal metabolism, a number of manganese-free substances were required, among them a suitable magnesium salt. In considering magnesium salts for this purpose, it was discovered that manganese was invariably present in all of the best and C. P. labeled magnesium salts and all other magnesium preparations obtainable. Also, all magnesium compounds especially prepared with reference to freedom from manganese contained the element. The presence of manganese could be demonstrated in all these magnesium preparations by both the periodate and the spectrographic methods. Furthermore, our own efforts showed that all known methods of purifying magnesium salts were ineffective for removing such traces of manganese as could be detected by either of the above methods. The idea was then conceived of removing the manganese by first converting it into permanganate. As is well known, this can be readily done by means of potassium periodate.

The first attempt to free magnesium from manganese in the permanganate form consisted of adding in the customary manner a small amount of potassium periodate to a 10% solution of magnesium sulfate acidified with sulfuric acid and heating the resulting solution until the pink permanganate color had developed. The solution was then cooled and rendered alkaline with ammonia. The resulting precipitate of magnesium