

the pure surgical cotton. The latter is easily explained by the difference in purity, the surgical cottons containing only 0.05 per cent. ash, the commercial cottons averaging 0.5 per cent. ash, but this is evidently quite immaterial for manufacturing purposes.

The varying results observed in manufacturing nitrocellulose, especially collodion cotton, must therefore *not* be attributed to variation in the quality of the cotton employed, but most probably to unequal conditions of nitration, perhaps as regards temperature, but most probably as regards differences in the percentages of water contained in the acid mixture, which may have been overlooked by the manufacturer. The preceding investigation shows that even very slight differences in the percentage of water may be of the greatest importance for the result, more important than even much greater differences in all other respects.

ZURICH, May, 1901.

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THE ELECTROLYTIC SEPARATION OF MERCURY FROM COPPER.

BY C. ROSCOE SPARE AND EDGAR F. SMITH.

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AT intervals, since the electrolytic separation of mercury from copper was first announced, statements have appeared that the separation was unsatisfactory. The first objection was to the length of time consumed, but it was soon observed in this laboratory that this factor was very materially reduced upon heating the electrolyte to 65° C. Then it was said that the separation was only applicable and satisfactory when the quantity of copper was not too large, as compared with the amount of mercury in the solution. Proper replies were made to these restrictions upon the method, but recently another chemist, in the person of Emil Goecke, published in his inaugural thesis "Ueber den Genauigkeitsgrad elektro-analytischer Arbeitsmethoden," etc., that he not only required from sixteen to twenty-four hours to effect the separation, but that in only three instances did he find the mercury free from copper. It is not the purpose of the writers to question Goecke's ability to conduct electrolytic work, or analytical work of any kind for that matter, but they feel that it is only fair to lay additional actual experience before the reader, leaving time and further trials to determine finally who is right.

In this laboratory the method in question has been so frequently carried out with success that it seemed almost useless to repeat ; but the following trials were undertaken and the results are presented in the order in which they were obtained. The details are sufficiently indicated in the tables.

TABLE.

In the approximate proportion of 1 Hg : 1 Cu.

Mercury. Gram.	Copper. Gram.	KCN. Grams.	Dilution. cc.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Gram.
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.03 A	{ 1.2 V 1.7 V	65°	3 ⁸ / ₁₆	0.1211
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.05 0.03 } ¹	{ 1.2 V 1.9 V	60°	2 ¹ / ₁₆	0.1208
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.2 V 1.5 V	63°	3 ³ / ₁₆	0.1211
1 Hg : 2 ¹ / ₂ Cu.								
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.2 V 1.5 V	65°	3 ¹ / ₁₆	0.1202
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.02 }	{ 1.2 V 1.5 V	65°	3 ¹ / ₁₆	0.1205
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.02 }	{ 1.2 V 1.5 V	65°	4	0.1210
1 Hg : 6 ¹ / ₂ Cu.								
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.012 }	{ 1.1 V 1.5 V	65°	2 ¹ / ₃	0.0453
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.02 }	{ 1.2 V 1.5 V	65°	3	0.0455
0.0453	0.3040	3.0	125	N.D. ₁₂₅ = 0.03 0.01 }	{ 1.1 V 1.5 V	60°	4 ¹ / ₄	0.0449
1 Hg : 11 Cu.								
0.0453	0.5115	6.0	135	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.2 V 1.5 V	65°	2 ² / ₃	0.0453
0.0453	0.5115	7.5	135	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.1 V 1.5 V	60°	3 ¹ / ₃	0.0447
0.0453	0.5115	5.5	135	N.D. ₁₂₅ = 0.03 0.01 }	{ 1.2 V 1.5 V	60°	2 ¹ / ₃	0.0454
3 Hg : 1 Cu.								
0.1211	0.0483	2.5	125	N.D. ₁₂₅ = 0.022 0.02 }	{ 1.5 V 1.5 V	60°	2 ³ / ₄	0.1210
0.1211	0.0483	2.3	125	N.D. ₁₂₅ = 0.03 0.01 }	{ 1.5 V 1.5 V	60°	4 ³ / ₄	0.1213
0.1211	0.0483	2.0	125	N.D. ₁₂₅ = 0.06 0.01 }	{ 1.6 V 1.5 V	65°	3	0.1205

¹ Maximum and minimum currents.

The deposit of mercury was, in each case, tested most carefully for copper, but the latter was never found. Why Goecke encountered the opposite experience we are not prepared to say. The only reagent used for washing was cold distilled water. The source of the electric energy was storage cells. The time factor here, as in numerous other experiments, is much reduced. From the abundance of evidence here presented on this topic and in former communications we are disposed to leave the controversy to those who delight in such occupation. We submit facts. They alone settle difficulties.

Goecke emphasizes the statement that carbon is present in metals deposited by the current from potassium cyanide solutions, "jedoch in so minimalen Mengen, dass dieselben für die Praxis kaum in Betracht kommen." Indeed, in but a single instance did it attain to 0.1 per cent., so that another writer has said "aber in so minimaler Menge, dass die Versuchsfehler der Bestimmungsmethoden kaum überschritten wurden." And we are disposed to add that in all probability a more thorough washing of the precipitated mercury would have removed the last traces of alkaline cyanide and the test for carbon would have resulted negatively.

One of the chief purposes of Goecke seems to have been the study of the impurities contained in metals precipitated on the cathode. He points to the occurrence of carbon in the iron deposited from a citrate solution. This fact was commented upon by the person who first precipitated iron from that electrolyte. It is an old story, and before long we shall very probably hear from Dr. E. F. Kern on this subject. He has executed a series of experiments showing upon what this co-precipitation of carbon is due and how it may be avoided. In time, too, we hope to speak of the occurrence of phosphorus in metals, deposited from solutions of phosphates. Goecke records it as an ever-present impurity in the metals deposited from such electrolytes.

But to return to the electro-deposition of mercury. The literature relating to this reveals the fact that very little experimentation in this way has been done with mercury in the presence of three or four other metals. Indeed, this is a direction in which investigation could be profitably conducted. We submit results obtained by us in following this thought.

Mercury. Gram.	Copper. Gram.	Cadmium. Gram.	KCN. Grams.	Dilution. cc.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Gram.
0.1211	0.1207	0.1410	4.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.04 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{Bmatrix} 1.4 \text{ V} \\ 1.5 \text{ V} \end{Bmatrix}$	65°	3 $\frac{1}{2}$	0.1204
0.1211	0.1207	0.1410	3.5	135	N.D. ₁₂₅ = $\begin{matrix} 0.04 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{Bmatrix} 1.2 \text{ V} \\ 1.5 \text{ V} \end{Bmatrix}$	65°	3 $\frac{1}{2}$	0.1211
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.02 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{Bmatrix} 1.4 \text{ V} \\ 1.5 \text{ V} \end{Bmatrix}$	65°	4 $\frac{3}{4}$	0.1207
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.03 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{Bmatrix} 1.3 \text{ V} \\ 1.5 \text{ V} \end{Bmatrix}$	60°	4 $\frac{1}{2}$	0.1203
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.04 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{Bmatrix} 1.4 \text{ V} \\ 1.5 \text{ V} \end{Bmatrix}$	60°	4	0.1208

Mercury. Gram.	Copper. Gram.	Cadmium. Gram.	Zinc. Gram.	KCN. Grams.	Dilution. cc.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Gram.
0.1211	0.1207	0.1410	0.1000	9.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.02 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{Bmatrix} 1.4 \text{ V} \\ 1.5 \text{ V} \end{Bmatrix}$	60°	5	0.1206
0.1211	0.1207	0.1410	0.1000	5.0	135	N.D. ₁₂₅ = $\begin{matrix} 0.03 \text{ A} \\ 0.01 \text{ A} \end{matrix}$	$\begin{Bmatrix} 1.5 \text{ V} \\ 1.5 \text{ V} \end{Bmatrix}$	60°	3 $\frac{3}{4}$	0.1207

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 58.]THE PRECIPITATION AND SEPARATION OF SILVER IN
THE ELECTROLYTIC WAY.

BY W. H. FULWEILER AND EDGAR F. SMITH.

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THE fact that silver can be quantitatively determined in the electrolytic way is well known. It has had ample confirmation in this laboratory, where numerous estimations of the metal in cyanide solution have been made. It is probable, too, that it was here that the first quantitative results with this electrolyte were obtained although it is customary to credit the method to Luckow notwithstanding, in his published account of the electro-deposition of silver from its double cyanide solution, he presents no quantitative data, and merely remarks in regard to such solutions: "So fällt aus solchen Lösungen das Silber gleichmässig in regulinischer form mit mattem Metallglanze nieder."¹ But be that as it may, without any further reference to the origin of the method, the latter is most deserving of consideration, and to

¹ *Ztschr. anal. Chem.*, 19, 15.