Advice & Counsel

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Training "Colombo"—Part XII
An Alternate Chloride Procedure

Dear Advice & Counsel,
Thank you for extending yourself to fly over and speak at our branch meeting. As in the past, your talk was extremely interesting and valuable.

As we discussed, I am sending you the chloride analysis method used at our facility. If you have any questions or comments, please contact me. Have a great week!

—Ron Barauskas
Technical Coordinator
Shipley Ronal

Dear Ron,
At a recent Golden West Regional meeting, you indicated that you had been following the Columbo series of articles and that you had an alternate procedure for determining the chloride content of an acid copper plating solution, using specific ion electrodes. At a more recent meeting at the Orange County Branch of AESF, you again reminded me of this procedure and I agreed that it was worthy of inclusion into our Training Columbo series, so here it is. Thank you, Ron, for the kind words on my presentation, and thank you (and Shipley Ronal) for sharing this procedure with our readers.

Check out the schedule of upcoming AESF courses on page 36.

Analysis for Chloride by Ion-specific Electrode Method of Additions

This method for chloride determination is not valid for samples with more than 1406 ppm chloride—the second value (V2) must be less than the initial value (V1).

Note: All equipment used for this analysis must be carefully rinsed in distilled or DI water (better than 10 megohm) in order to avoid chloride contamination. The 150-mL beakers must be also dry when the sample is introduced.

1. Pipette a 100-mL sample into a 150-mL beaker. Add a magnetic stir bar.
2. Immerse the chloride-specific ion electrodes (**Note:** they must be properly prepped—see instructions with the electrodes; rinse with DI water and dry with tissue). Warning: Never touch the bottom portion of the electrodes with bare fingers. Turn on the magnetic stirrer. Turn the pH function switch to millivolts-expanded scale. Note: The instrument must be capable of reading to 0.1 mV.
3. Pipette 2 mL of 5M $NaN0_3$ (424 g/L) into the sample and allow the reading to stabilize. A reading should hold for one minute (to 0.1 mV). Record that value as V1.
4. Pipette 5 mL of a 1.5 g/L chloride standard. (Weigh out 1.2364 g + 0.0002 of reagent grade sodium chloride and dilute to 500 mL).
5. Allow the reading to stabilize (if reading does not stabilize in five minutes, the electrodes may not be prepped properly, so they should be re-prepped). Record this value as V2.
6. ΔE = V2 - V1 (ignore the sign of the difference between V2 and V1—*i.e.*, use the absolute value).
7. Locate the ΔE value in the table and read off the ppm chloride.

How to Use the Table

To use the table, obtain the ΔE in mV from step 6. Find the integer (to the left of the decimal point) in the left-most column and the tenths digit (to the right of the decimal point) on the top row. The intersection of the row and column gives the value of chloride in ppm. Example: ΔE = 20.2. Find 20 in the left-most column and 2 on the top row. They intersect at 53.3 ppm chloride.

The equation used to generate this table is:

$$Cx = \frac{(0.049)\ (1500)\ ((100 + 2)/100)}{-(1(1 + 0.049)\ (10^{\Delta E/56}))}$$

or

$$Cx = \frac{74.97}{-1(1-(1.049)(10^{\Delta E/56}))}$$

Table for Chloride Determination

Note: The table provided by Ron Barauskas allows determination of chloride from 1.2-1406 ppm, and is three pages long. For publication, we have abbreviated it to the typical range of chloride found in most acid copper solutions (30-100 ppm). The reader may contact Ron or me for the full table.

ΔE	**.0**	**.1**	**.2**	**.3**	**.4**	**.5**	**.6**	**.7**	**.8**	**.9**
12	104.4	103.4	102.4	101.4	100.4	99.4	98.5	97.6	96.6	95.8
13	94.9	94.0	93.1	92.3	91.4	90.6	89.8	89.0	88.2	87.4
14	86.6	85.9	85.1	84.4	83.6	82.9	82.2	81.5	80.8	80.1
15	79.4	78.8	78.1	77.5	76.8	76.2	75.6	74.9	74.3	73.7
16	73.1	72.5	71.9	71.4	70.8	70.2	69.7	69.1	68.6	68
17	67.5	67.0	66.5	66.0	65.4	65.0	64.5	64.0	63.5	63.0
18	62.5	62.0	61.6	61.1	60.7	60.2	59.8	59.4	58.9	58.5
19	58.1	57.6	57.2	56.8	56.4	56.0	55.6	55.2	54.8	54.4
20	54.0	53.6	53.3	52.9	52.5	52.2	51.8	51.4	51.1	50.7
21	50.4	50.0	49.7	49.4	49.0	48.7	48.4	48.0	47.7	47.4
22	47.1	46.8	46.5	46.2	45.8	45.6	45.2	45.0	44.7	44.4
23	44.1	43.8	43.5	43.2	42.9	42.7	42.4	42.1	41.8	41.5
24	41.3	41.1	40.8	40.5	40.3	40.0	39.7	39.5	39.3	39.0
25	38.8	38.6	38.3	38.1	37.8	37.6	37.4	37.2	36.9	36.7
26	36.5	36.2	36.0	35.8	35.6	35.4	35.2	35.0	34.7	34.5
27	34.3	34.1	33.9	33.7	33.5	33.3	33.1	32.9	32.7	32.5
28	32.4	32.2	32.0	31.8	31.6	31.4	31.2	31.0	30.9	30.7