Colorimetric Determination of Iron

In the Presence of Large Concentrations of Copper and Nickel

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The usefulness of disodium-1,2-dihydroxybenzene-3,5-disulfonate as a chromogenic reagent for the determination of iron has been extended. A technique has been applied which allows estimation of iron in the presence of large quantities of copper and nickel. As little as 0.025% iron in blue vitriol can be estimated without prior separations.

YOE and Jones (2) proposed the use of disodium-1,2-dihydroxybenzene-3,5-disulfonate (tiferron) as a colorimetric reagent for the estimation of ferric iron. They found that comparatively large concentrations of a number of diverse ions offer no interference, but that, in the presence of 1.0 p.p.m. of iron, the copper concentration must be less than 25.0 p.p.m.

In the writer's laboratory, iron determinations are made on a considerable number of liquors incident to the electrolytic refining of copper. These liquors contain comparatively small amounts of iron in the presence of sulfuric acid, arsenic, antimony, up to 18% copper, and up to 8% nickel. In addition, small percentages of iron are determined in blue vitriol samples.

A method which would permit iron estimations without prior separations of the copper and nickel would have obvious advantages. Silverthorn and Curtis (1) determined chromium in the presence of manganese which interferes at the wave length employed. They measured the total absorption caused by the manganese and chromium together and then corrected for the light absorbed by the manganese alone. Standard curves were used for this purpose.

It was the purpose of this investigation to attempt to devise a method for estimating iron in the presence of arsenic, antimony, nickel, and copper, using the technique of Silverthorn and Curtis as a basis and tiferron as the chromogenic reagent.

APPARATUS

All the optical measurements were made with a Coleman model 11 Universal spectrophotometer having a band width of 35 mμ. Cylindrical glass cells having an inside diameter of 16 mm. were employed.

SOLUTIONS

TIFERRON. This reagent was obtained from LaMotte Chemical Products Co. An aqueous solution containing 25 grams per liter was used.

BUFFER. This solution contained 20 grams of sodium hydrogen carbonate and 10 grams of sodium carbonate per liter of solution, twice the strength of the buffer used by Yoe and Jones (2). The stronger solution was used in order to obtain the proper pH with test aliquots containing sulfuric acid.

STANDARD IRON. Analytical grade iron wire was dissolved in dilute hydrochloric acid. The solution was oxidized with bromine water and the excess expelled by boiling. The solution was made up to 1 liter and used as a stock solution.

STANDARD NICKEL. A stock solution was made from reagent grade nickel sulfate crystals having an iron concentration of 0.0005%. Its exact strength was determined electrolytically.

STANDARD COPPER. A stock solution was made from reagent grade copper sulfate pentahydrate crystals. Exact strength was determined electrolytically. Crystals contained 0.00035% iron.

GENERAL PROCEDURE

Transfer a suitable aliquot to a 50-ml. volumetric flask and add enough tiferron solution to take care of all the copper, nickel, and iron present. Mix, dilute to the calibration mark with the buffer solution, and mix thoroughly. Transfer a portion of the solution to an absorption cell and measure the light transmittancy

at 500 mμ, using water as the reference solution. Readings should be taken within 4 minutes following the addition of the buffer solution. The per cent iron is read from tables, prepared as described below.

The procedure presupposes some knowledge as to the approximate concentrations of copper and nickel in the sample. If the nickel content is not more than sixty times that of the iron, its effect may be neglected.

The minimum quantity of tiferron required for the test is determined by the amounts of iron, copper, and nickel present. Experiments have shown that in terms of dry tiferron, the respective requirements for 1 part of iron, 1 part of copper, and 1 part of nickel are 40, 12, and 1.25 parts. These quantities are somewhat in excess of minimum requirements. It has been found that an excess of the reagent has no effect in the presence of copper and iron but does influence the results to a negligible extent when nickel is present. A large excess of the reagent should be avoided because of its cost.

WAVE LENGTH-TRANSMITTANCY RELATIONS

The wave length–transmittancy characteristics for iron, copper, and nickel are shown in Figure 1. The respective concentrations used for these tests were 0.050, 15.0, and 49.0 mg. per 50 ml.

It will be noted that the shapes of the nickel and copper curves are similar and differ from that of the iron curve. The maximum absorption for iron corresponds to a wave length of about 490 mμ, which is close to the 500 established for the testing work. The absorption minima for copper and nickel are in the neighborhood of 550 mμ.
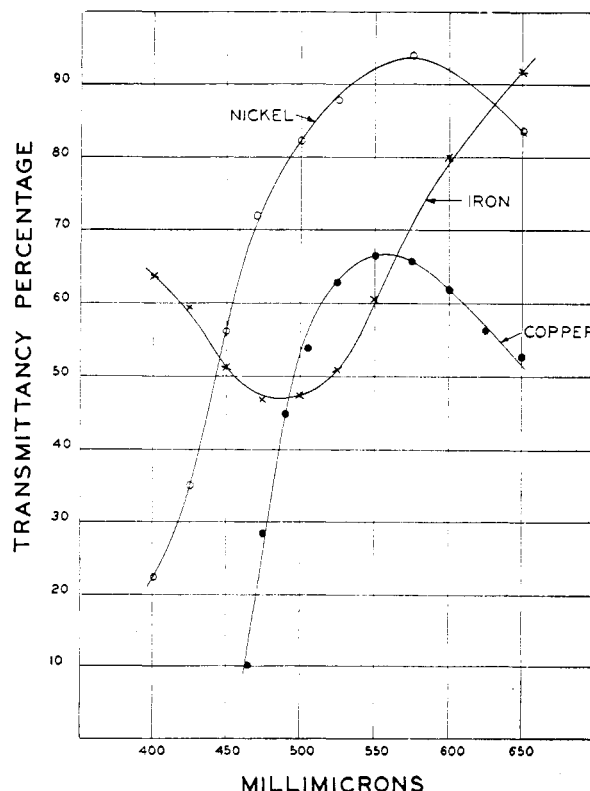

Figure 1. Transmittancy Curves for Nickel, Iron, and Copper

Table I. Aliquot Schedule

Type of Material	Initial Sample Weight	Dilution Volume	Volume of Aliquot	Volume of Ti-ferron	Use Sched-ule
	Grams	Ml.	Ml.	Ml.	
A liquor	5.0	200	2.0	12	A
B liquor	5.0	200	1.0	2	B
C liquor	5.0	200	1.0	2	B
D liquor	5.0	200	2.0	8	A
E liquor	5.0	200	1.0	2	B
Blue vitriol	25.0	500	2.0	14	C

Table II. Iron Schedule

% Transmittancy	% Iron		
	4% Cu	6% Cu	8% Cu
	Schedule A, A and D liquors		
50	0.148	0.136	0.122
49	0.154	0.142	0.128
48	0.160	0.148	0.134
47	0.165	0.153	0.139
	Schedule C, Blue Vitriol		
	24% Cu	25% Cu	26% Cu
25	0.045	0.040	0.035
24	0.050	0.045	0.040
23	0.056	0.051	0.046
22	0.062	0.057	0.052
21	0.069	0.064	0.059

CONCENTRATION-TRANSMITTANCY RELATIONS

The concentration–transmittancy relations were investigated for copper, nickel, and iron at 500 mμ (Figure 2). The procedure outlined above was followed, using varying quantities of the standard solutions.

The curves cut the vertical axis at a point representing 96.5% transmittancy instead of the expected 100%, because water, rather than a blank containing the buffer and tiferron, was used as the reference solution.

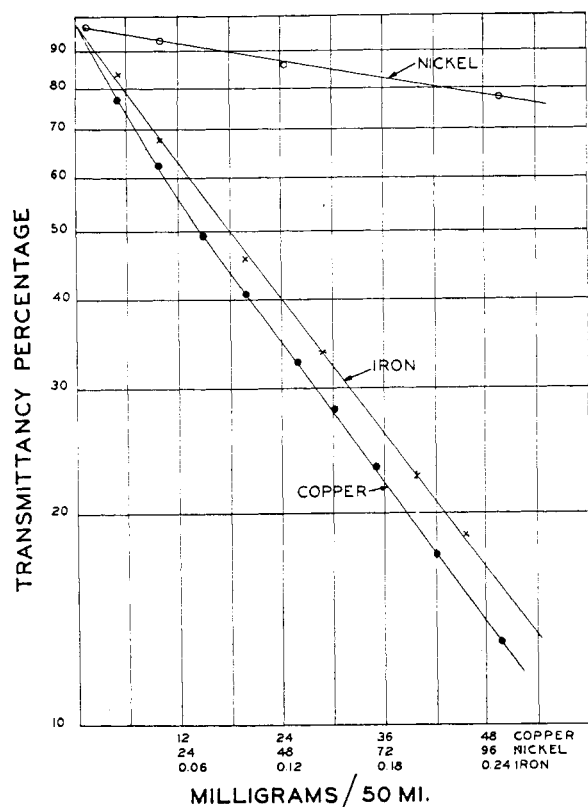It will be seen that Beer's law holds for nickel and iron, while

Figure 2. Transmittancy-Concentration Curves for Nickel, Iron, and Copper

there is a considerable deviation corresponding to the lower concentrations of copper.

The absorption by the nickel complex is comparatively low and its effect may be neglected with respect to lower concentrations.

At higher nickel concentrations, corrections should be applied for the nickel present. The method outlined below for copper can be used. Because of the increase in light absorption with time, readings should be taken within 4 minutes after addition of the buffer as recommended in the general procedure.

The colors developed by copper and iron are relatively stable, no material change in transmittancy taking place over the first half hour.

Comparatively high concentrations of arsenic and antimony, both trivalent and quinquevalent, showed no light absorption at 500 mμ. No further consideration has, therefore, been given these elements.

CORRECTION FOR COPPER PRESENT

The presence of copper in a sample will manifest itself by an increase in the light absorbed, resulting in an apparent increase in the concentration of iron. Readings must therefore be corrected for the copper present.

This may be done by referring to the copper curve in Figure 2 and noting the transmittancy corresponding to the known copper concentration. Reference is then made to the iron curve, and the iron concentration corresponding to this transmittancy is the correction for the copper present. This correction is subtracted from the total apparent iron equivalent to the actual instrument reading. The difference is equal to the true iron concentration.

An example will make this clear. Assume that an aliquot contains 12 mg. of copper and that the instrument reading is 40. Reference to the copper curve in Figure 2 shows that the percentage transmittancy corresponding to 12 mg. of copper is 56. Reference to the iron curve shows that 56% transmittancy is equivalent to 0.074 mg. of iron. The apparent iron equivalent to the actual instrument reading of 40% is 0.12 mg. The true iron content is then 0.12 − 0.074 or 0.046 mg.

As an aid in routine work, a table has been arranged to cover some of the samples tested in the author's laboratory showing the dilution, size of aliquot to be taken, and volume of tiferron to be used. In addition, tables have been assembled to show the concentration of iron corresponding to various instrument readings and corrected for a number of different copper concentrations. Abbreviated forms are represented by Tables I and II.

CHECKS ON KNOWN MIXTURES

Some determinations were made on "synthetic" mixtures containing varying quantities of copper, nickel, and iron (Table III).

The results of determinations made on some production materials whose iron contents had previously been determined gravimetrically are shown in Table IV.

In making these determinations, a quantity of the sample was transferred to a beaker, diluted with water, and 5 ml. of 1 to 4

Table III. Iron Checks on Synthetic Mixtures

Composition of Mixture			Fe Found
Cu	Ni	Fe	
	Mg./50 ml.		Mg./50 ml.
6	1.44	0.060	0.058
8	1.44	0.030	0.031
10	0.028	0.010	0.018
10	0.028	0.030	0.040
15	2.80	0.050	0.052
20	0.056	0.020	0.025
20	0.056	0.030	0.034
20	0.056	0.060	0.063
30	0.112	0.010	0.018
30	0.112	0.030	0.040
30	0.140	0.070	0.068
30	0.140	0.090	0.090
30	0.140	0.100	0.100
30	1.40	0.070	0.071
30[a]	14.00	0.070	0.075
30[a]	49.00	0.070	0.070
30[a]	98.00	0.070	0.070

[a] Corrected for nickel present.

Table IV. Iron Checks on Materials in Process

Type of Material	Approximate Percentage				Percentage of Fe Gravi-metric	Colori-metric
	As	Sb	Cu	Ni		
H-3 liquor	0.2	0.03	2.70	0.70	0.024	0.023
H-3 liquor	0.2	0.03	2.67	0.74	0.025	0.025
H-3 liquor	0.2	0.03	2.70	0.72	0.028	0.031
H-4 liquor	0.2	0.03	1.75	0.82	0.025	0.025
H-4 liquor	0.2	0.03	1.71	0.85	0.028	0.027
H-4 liquor	0.2	0.03	1.95	0.82	0.038	0.034
H-5 liquor	0.2	0.03	2.64	0.65	0.021	0.019
H-5 liquor	0.2	0.03	2.92	0.67	0.022	0.020
O liquor	0.6	..	15.20	0.40	0.054	0.050
A liquor	1.2	..	15.70	1.70	0.230	0.215
E liquor	2.8	..	3.80	4.50	0.416	0.365
G liquor	0.3	0.08	3.00	..	0.024	0.023
Blue vitriol	...	..	25.1	..	0.032	0.025
	...	..	25.1	..	0.025	0.020
	...	..	25.1	..	0.026	0.024
	...	..	25.1	..	0.026	0.027
	...	..	25.1	..	0.070	0.063
	...	..	25.1	..	0.086	0.080

sulfuric acid were added to prevent the precipitation of arsenic and antimony. A few milliliters of saturated bromine water were then added and the excess was expelled by boiling. The solution was cooled, and if the acidity was initially high it was neutralized by means of ammonium hydroxide, and a slight excess of 1 to 4 sulfuric acid added. The test was again cooled, transferred to a volumetric flask, diluted to the mark, and thoroughly mixed. An aliquot was transferred to a 50-ml. volumetric flask and the general procedure outlined above was followed.

DISCUSSION

Iron may be determined in the presence of large quantities of copper and nickel with excellent accuracy, provided the iron concentration is not less than 0.05 mg. per 50 ml. Below this concentration, the expected error is somewhat greater but will still be sufficiently small for many purposes.

The iron was accurately determined in a "synthetic" mixture containing 30 mg. of copper, 98 mg. of nickel, and 0.070 mg. of iron per 50 ml. In this case it was necessary to correct for both the copper and nickel present.

The maximum concentration of nickel which may be present in a mixture is probably much higher than the maximum reported on in this investigation. In such cases, it would be necessary to take transmittancy readings very quickly following addition of the buffer solution.

It is believed that the utility of many of the published spectrophotometric analytical methods can be extended materially by the use of corrected tables similar to those described in this paper. The author is now applying this technique to the estimation of small concentrations of nickel in samples of the type shown in Table IV and expects to publish the findings at a later date.

LITERATURE CITED

(1) Silverthorn, R. W., and Curtis, J. A., *Metals and Alloys*, 15, 245 (1942).
(2) Yoe, J. H., and Jones, A. L., IND. ENG. CHEM., ANAL. ED., 16, 111 (1944).

Destruction of Organic Matter in Blood Fibrin and Chromacized Medical Catgut by Wet Oxidation

Determination of Iron in Blood and of Chromium in Sutures

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THE determination of the mineral components of blood and the evaluation of chromium in chromacized medical catgut sutures are generally carried out starting with a dry-ashing procedure. This operation is time-consuming. Subsequent to dry-ashing at elevated temperatures the residue may require a fusion process to redissolve the ash. For these reasons a wet-ashing procedure is recommended and herein described.

The literature on the use of mixtures of nitric and perchloric acids in the wet-oxidation of organic matter preparatory to the determination of sulfur, phosphorus, and arsenic as well as the metallic components iron, chromium, aluminum, calcium, magnesium, sodium, and potassium has been previously surveyed (4, 7). The important applications are the determination of sulfur in coal (9), chromium in leather (3), iron in leather (6), calcium, phosphorus, and the alkali metals in plant materials (1), sulfur in organic compounds (4), and iron in wine or beer (7).

CHEMICAL ASPECTS OF WET-OXIDATION ACID MIXTURES CONTAINING PERCHLORIC ACID

Because perchloric acid is known, when hot and concentrated, to exert a powerful oxidizing effect in contact with organic matter, its use for wet-ashing purposes is retarded by unwarranted apprehension of violent reactions. When properly used for wet-mineralization of samples composed preponderantly of organic matter, perchloric acid is entirely dependable. Samples of heterocyclic ring nitrogen compounds such as occur in coal which are oxidized with great difficulty by hot concentrated sulfuric acid, as in the Kjeldahl reaction, are readily and rapidly oxidized by mixtures of nitric acid and perchloric acid; vanadium must be used as catalyst to speed the oxidation to a time limit of 15 minutes (9).

The use of mixtures of concentrated nitric and perchloric acids as oxidants for organic materials of a wide variety of sources gives smooth, easily controlled, suitably rapid reactions because the mixture exerts a gradually increasing oxidation potential. The addition of concentrated nitric acid to concentrated (72%) perchloric acid dilutes the latter acid, which lowers its oxidation potential. At the same time the concentration of nitric acid, owing to its partial dehydration by the perchloric acid, increases its strength and oxidation potential. The mixed acids may be applied at ordinary temperatures and their oxidation effects gradually increased by elevating the temperature. The more easily oxidized portions of the organic matter are first attacked. As the temperature is raised the nitric acid excess is finally distilled off and the diluted perchloric acid begins to concentrate, and finally at 200° C. attains a constant boiling mixture (72% perchloric acid). During the course of this process its oxidation potential increases and the organic matter present which has escaped the nitric acid attack is gradually oxidized by the perchloric acid. The more easily oxidized organic material is destroyed by hot 60% perchloric acid and the most difficultly destroyed organic matter is finally oxidized by the boiling 72% perchloric acid, quietly and efficiently.

The most outstanding property of a mineralization reaction following mixed nitric-perchloric acid digestion at gradually elevated temperature is the fact that the organic matter is destroyed without accompanying carbonization, which is so pre-