Determination of Copper in Lead and Lead Base Alloys

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ABSTRACT

This work was undertaken in an effort to develop a rapid method for the determination of copper in the range of 0.01 to 0.05% in lead alloys and in the range of 0.001 to 0.005% in lead. A visual and a photometric method are suggested, based on the color developed by copper in concentrated hydrochloric acid. Iron interferes with the determination, but this interference is reduced by use of an aluminum file in the visual method, and is corrected for in the photometric method by determination of the iron as the thiocyanate. The visual method is very rapid, is accurate to plus or minus 0.1% in the range 0.01–0.05%, and is suggested as a control method for alloys. The photometric procedure is accurate to better than 0.005% in the range of 0.01 to 0.05% and 0.0005% in the range 0.001 to 0.005%, and is suggested as a routine or control method.

Studies of the chloro complexes of copper in aqueous solution have been made by several investigators (2,4,5, 7,9), and one absorbing complex of copper has definitely been established as the CuCl[(2)] ion. Huttner (6) determined copper in hydrochloric acid by comparing the color with standard copper solutions, using a colorimeter. He found that the intensity of color produced by any given concentration of copper was not affected by variations in the concentration of hydrochloric acid, provided the percentage of hydrogen chloride was at least 28.0%. Several quantitative colorimetric methods for copper using the color produced by a cupric halide have been reported (1,3,6,8), and in each of these the interference due to iron was corrected for, if necessary. In the present investigation the colors produced by copper and iron in concentrated hydrochloric acid have been studied and applied to the determination of copper in lead and lead alloys.

Equipment and Reagents

Colorimeter: — A Bausch & Lomb Monochromatic Colorimeter with filters of 430 mu and 505 mu was used. Matched ½ inch test tubes were used for the sample containers.

Centrifuge: — An International Size 2 Centrifuge was used.

Aluminum file: — An aluminum file was made by knurling a rod of Alcoa aluminum alloy (61S-T6). The rod was ½ inch in diameter and 12 inches long.

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[2]Our font lacks the symbol used by the authors; what is meant is the tetrachlorocuprate II-ion. *Ed.*

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Reagents: — All reagents used conformed to ACS specifications.

Hydrochloric acid-bromine (saturated) :—An excess of bromine was added to 2 liters of concentrated hydrochloric acid, and allowed to stand at least twenty-four hours, with occasional mixing.

Ammonium Thiocyanate (115 g./1.).—One hundred and fifteen grams of ammonium thiocyanate were dissolved in 300 ml. of distilled water, filtered, diluted to 1 liter and stored in a dark bottle.

Hydrogen Peroxide (3%) :—Ten milliliters of H_2O_2 (30%) were diluted to 100 ml. and stored in a dark bottle.

Experimental Procedures

Visual Method

Standards.—Bureau of Standards sample number 53c, lead base bearing metal, which contain 0.215% copper, was used to prepare the standards for visual comparison. Samples of this alloy (which contained weights of copper corresponding to the weights in 0.500 g. samples of alloys having copper percentages of 0.01, 0.02, 0.03, 0.04, and 0.05) were weighed, transferred to 150-ml. beakers, and dissolved by boiling in approximately 40 ml. of hydrochloric acid-bromine until no more brown fumes were visible. After removal from the hot-plate, 0.2 g. sodium sulfite was added to expel the balance of the bromine, 1 ml. of glacial acetic acid added to keep the lead in solution, the solutions diluted to 50 ml. with concentrated hydrochloric acid, and cooled to room temperature.

Determination.—All samples were taken with the aluminum file, since use of this file eliminated the possibility of introducing ferric oxide which would interfere in the determination.

A 0.500 g. sample of lead alloy was transferred to a 150-ml. beaker and treated the same as the visual standards. The concentration of copper was determined by visual comparison with the standards against a white background. It was found that the samples should pass a 60-mesh screen in order for the alloy to dissolve before the bromine was expelled completely. Larger particle sizes greatly increased the time necessary for solution of the samples.

Photometric Method

The absorption curves of copper in concentrated hydrochloric acid, and of iron in concentrated hydrochloric acid, were run by the usual method using a Beckman DU Spectrophotometer and Corex cells with ground glass stoppers. The maximum absorption of copper was found to be at 380 mu and that of iron at 365 mu.

At wave lengths close to these maxima, we found that the absorptions for copper and iron were not additive in solutions which contained both ions. At 430 mu, however, the absorptions were approximately additive and this wave length was chosen for the measurements. It was also found that a correction could be applied for the presence of iron, provided the absorption of the mixture was determined at 430 mu; and the iron was then determined in an aliquot of the solution by the thiocyanate method.
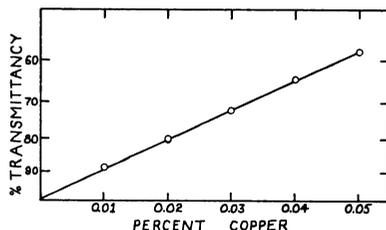

FIGURE 1

Standard Copper Curve.—Bureau of Standards sample number 53c was also used to prepare the standard copper curve for the photometric method. Samples of this alloy which contained weights of copper corresponding to the weights in 2.500 g. samples of alloys having copper percentages of 0.01, 0.02, 0.03, 0.05, and 0.05 were weighed, transferred to 150-ml. beakers, and dissolved in a mixture of 5.0 ml. of concentrated nitric acid and 15.0 ml. of concentrated hydrochloric acid. The samples were heated to speed solution, and more hydrochloric acid was added if necessary to keep the tin and antimony in solution. Ten ml. of sulfuric acid (1 to 1) was added to each sample, the solutions diluted to approximately 40 ml., and boiled to convert all lead chloride to lead sulfate. The solutions were then cooled, transferred to 50-ml. centrifuge tubes, and centrifuged for two minutes at 2300 r.p.m. The solutions were decanted into 150-ml. beakers, the precipitates washed once by centrifuga-

tion with 5 ml. of distilled water, and the combined centri-
fugates for each sample evaporated to strong fumes of sul-
fur trioxide. The solutions were cooled, transferred with
concentrated hydrochloric acid to 50-ml. volumetric flasks,
diluted to the mark with concentrated hydrochloric acid,
and the transmittancy was read at 430 mu. The Standard
Copper Curve is shown in Figure 1.

Iron Correction Curve.—A standard iron solution was
used to prepare the iron correction curve. Volumes of this
solution which contained amounts of iron corresponding to
the weights in 2.500 g. samples of alloys having iron per-
centages of 0.01, 0.02, 0.03, 0.04, and 0.05 were measured
into 50-ml. volumetric flasks, made up to volume with con-
centrated hydrochloric acid, and the transmittancies deter-
mined at 430 mu. Volumes of 20.00 ml. of these solutions
were then pipetted into 250-ml. volumetric flasks. Added in
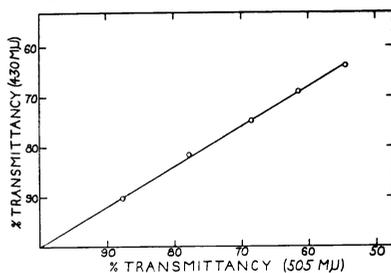order with mixing were 100 ml. of distilled water, 1.5 ml.

FIGURE 2

of 3% hydrogen peroxide, and 50 ml. ammonium thiocyanate
(115 g./1.). The solutions were diluted to the mark and the
transmittancies at 505 mu determined. A blank was run
using 20.00 ml. of concentrated hydrochloric acid. The per-
cent transmittancy of the iron in hydrochloric acid was
plotted against the percent transmittancy of the iron by
thiocyanate and is shown in Figure 2.

Determination.—A 2.500 g. sample was transferred to a
150-ml. beaker and treated in the same manner as in the
procedure for the Standard Copper Curve. After the reading
at 430 mu was obtained, 20.00 ml. of the solution was pip-
etted into a 250-ml. volumetric flask and the iron determined
by thiocyanate. The correction for iron was made by sub-
tracting the percent transmittancy of the iron in hydro-
chloric acid, as read from the correction curve, from 100

and adding this difference to the value obtained at 430 mu. The percent copper was then read from the Standard Copper Curve.

Results

The results of several determinations by the visual and photometric method are shown in Table 1. The visual method may be used as a rapid control determination of copper in amounts between 0.01 and 0.05% with an accuracy of approximately 0.01% copper.

To check the photometric method, varying amounts of standardized copper and iron solutions were added to samples of Bureau of Standards sample 127, solder (65-35). It was found that when the percent of copper is 0.03% or more, the iron must be less than 0.01% to prevent interference.

To determine the amount of copper in pure lead, the sample weight was increased to 12.50 g. and run in the same way as the lead alloys. These results are shown in Table 1.

TABLE I

Sample	Southern Lead Co. No.	Analysis	Percent Cu Found Visual	Photometric
Antimonial				
Grid Metal	3227	0.036	0.05	0.040 ± 0.002
"	3234	0.033	0.04	0.035 ± 0.003
"	3243	0.011	0.02	0.020 ± 0.002
"	3233	0.047	0.05	0.048 ± 0.003
Antimonial Sleeving Met.	3246	0.051	0.05	0.049 ± 0.001
"	3238	0.059	0.05	0.059 ± 0.001
B. of S. 127 Solder, 65-35	---	0.014*	0.01	0.015 ± 0.001
Pure Lead	862	0.0030	---	0.0033 ± 0.0001
"	858	0.0025	---	0.0024 ± 0.0002
"	880	0.0042	---	0.0046 ± 0.0002

*Bureau of Standards analysis

Discussion

It was found that the addition of hydrochloric acid to keep the tin and antimony in solution was necessary, since some copper is lost when these are removed as precipitates when the samples were dissolved in nitric acid. Seven determinations of Bureau of Standards sample number 126 were made by dissolving the samples in nitric acid only and gave an average value of 0.006 ± 0.001%. Fifteen determinations made by dissolving the same alloy in a mixture of

hydrochloric and nitric acids gave an average value of 0.015 ± 0.001%. The correct value is 0.014%.

The photometric method for copper may be applied to lead and lead-base alloys if the copper content is from 0.001 to 0.005% or from 0.01 to 0.05%. The method is accurate to better than 0.005% copper in the range 0.01 to 0.05% and better than 0.0005% in the range 0.001 to 0.005%.

The visual method is very rapid and is accurate to ±0.01% copper in a 0.50 sample.

Acknowledgment

The authors express their appreciation to Mr. Jack Pinkston of Southern Lead Co., Dallas, for furnishing samples for analysis.

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New Names for Texas Leguminosae

B. L. Turner

Mimosa **warnockii** nom. nov.—*Mimosa flexuosa* Benth. ex Gray, Pl. Wright. 1:62. 1852. Not *M. flexuosa* Poir., Encyc. Supp. 1:79. 1810. A small shrub 1—(3) feet tall, forming neat, dome-shaped clumps on the rolling, igneous footbills and flats of the Davis Mountains, north of Marfa, Texas. The species is related to *M. biuncifera* and is sometimes included as a variety of that species. In the field and on herbarium sheets the taxa are clearly distinct and so far as known do not intergrade. *M. warnockii* is named for Dr. Barton H. Warnock of Sul Ross State College, Alpine, Texas, who first showed me the extensive populations of the plant in the field and pointed out the salient characters which separate it from *M. biuncifera*.

Mimosa pigra L. var. **berlandieri** (Gray) comb. nov.— *Sophora sericea* Nutt., Gen. Am. 1:280. 1818. Not *S. sericea* Andrews, Bot. Rep. t. 440. 1806[1]. The first published description for any portion of *S. nuttalliana* was apparently made

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[1] I am grateful to Rupert Barneby, Dr. Reed C. Rollins and Dr. Lloyd Shinners for offering critical advice concerning the nomenclature of this species.