

## The Determination of Copper in Certain High-alloy Steels

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A modified method for the determination of copper in certain high-alloy steels has been developed. Separation is based on the extraction of copper dithizonate with carbon tetrachloride, copper being finally determined absorptiometrically as its blue *biscyclohexanone oxalyldihydrazone* complex. The range of copper concentration covered by the method is about 2 to 10 per cent., but this can be extended in either direction by adjusting the sample weight or the aliquot of solution used in the extraction.

THE procedure described in this paper was devised in order to provide an accurate means of determining copper in certain high-alloy steels. Methods in which *biscyclohexanone oxalyldihydrazone* is used for the determination of copper in ferrous materials have been described by Haywood and Sutcliffe<sup>1</sup> and Wetlesen.<sup>2</sup> We have successfully used Haywood and Sutcliffe's procedure to determine copper in a range of low-alloy and mild steels, but, when the method was applied to the analysis of permanent-magnet alloys and stainless steels, a significant fading of the blue colour was observed, especially with the magnet alloys. Previous workers<sup>1,2</sup> have recorded that iron produces a background colour under the experimental conditions, which is compensated for by the blank solution, and that hexavalent chromium does not cause any significant interference. Wetlesen<sup>2</sup> noted that large amounts of cobalt and nickel cause a negative interference, and consequently it was simple for us to confirm that these two metals were the cause of the fading in our experiments. We were able to show that cobalt was responsible for a more serious error than nickel and that, for the magnet alloys, the average order of the fading was about 5 to 7 per cent. of the theoretical optical density in 30 minutes. Optical density - time graphs were plotted and it was shown that the theoretical optical density was obtained if the graphs were projected to zero time. Consequently, the error caused by fading can be reduced by measuring the optical density of the solution as soon as possible after colour development is complete. This expedient is only a partial solution to the problem and cannot conveniently be resorted to when analyses are being carried out in batches or when results of the highest accuracy are required. In order to overcome the problem of fading, attempts were made to introduce a suitable separation procedure. The use of a dithizone extraction stage has permitted us to modify the method successfully.

### EXPERIMENTAL

Solvent-extraction procedures were reviewed, and it appeared that copper could be selectively extracted, as its dithizone complex,<sup>3</sup> from a solution of the steel in dilute acid. Attempts to determine copper directly by measuring the optical density of the extract were unsuccessful, as dithizone absorbs strongly in the same waveband as the copper complex and the mixed-colour method is not sufficiently accurate. It is possible to remove excess of dithizone by means of an aqueous ammoniacal solution, but this results in the loss of some copper by partial keto - enol transformation in the complex.<sup>4</sup> Consequently, it was impossible to use a direct measurement on the carbon tetrachloride extract.

A modification of the method was therefore required, and, provided that iron, cobalt and nickel were not co-extracted to any significant extent with the copper dithizonate, it appeared that the *biscyclohexanone oxalyldihydrazone* complex could be used. Tests were carried out to determine the behaviour of these three metals. Solutions of 0.1-g samples of a synthetic alloy of iron, cobalt and nickel (1 + 1 + 1) were prepared and extracted in exactly the same way as for the removal of copper from a solution of a steel. The resulting organic extract was analysed for copper and nickel by polarography and for iron by absorptiometry, and it was shown that the concentrations of all three metals were in the range 0.01 to 0.1 p.p.m.

It was therefore clear that *biscyclohexanone oxalyldihydrazone* could be used to determine copper after separation as its dithizonate. It was simple to destroy the organic ligand with an oxidising acid mixture before the blue colour of the copper complex was developed.

## METHOD

## REAGENTS—

*Nitric acid, diluted* (1 + 3).

*Sulphuric acid, sp.gr.* 1.84.

*Carbon tetrachloride.*

*Dithizone solution*—Prepare a 0.05 per cent. solution of dithizone in carbon tetrachloride.

*Oxidising acid mixture*—Mix 1 volume of sulphuric acid, sp.gr. 1.84, 1 volume of nitric acid, sp.gr. 1.42, and 2 volumes of perchloric acid, sp.gr. 1.70.

*Citric acid solution*—Prepare a 25 per cent. w/v solution of citric acid in water.

*Ammonia solution, sp.gr.* 0.880.

*$\alpha$ -Naphtholphthalein indicator solution*—Prepare a 0.1 per cent. solution of the indicator in 50 per cent. aqueous ethanol.

*Biscyclohexanone oxalyldihydrazone solution*—Prepare a 0.5 per cent. solution of the reagent in 50 per cent. aqueous ethanol.

*Standard copper solution*—Prepare a solution containing 1 mg of copper per 10 ml by dissolving spectrographically pure copper in diluted nitric acid (1 + 1). The final solution used was approximately 0.1 *N* with respect to nitric acid.

## PROCEDURE—

Dissolve 0.1 g of alloy in 10 ml of diluted nitric acid (1 + 3) in a 125-ml beaker. (For samples of stainless steel, use 50 ml of diluted sulphuric acid (1 + 4), and oxidise residual carbides with about 5 ml of nitric acid, sp.gr. 1.42.) Cool the solution, and carefully add 10 ml of sulphuric acid, sp.gr. 1.84, except for samples of stainless steel, when no further sulphuric acid need be added. Cover the beaker with a watch-glass, heat until fumes of sulphur trioxide are evolved, cool to room temperature, and dilute to 500 ml in a calibrated flask. Transfer 10 ml of the resulting solution to a 100-ml separating funnel, and dilute to 30 ml. (If the sample contains less than about 2 per cent. of copper, take a larger aliquot, and dilute accordingly to the correct acidity, 0.1 to 0.5 *N*.)

Extract successively with 30-ml and 5-ml portions of 0.05 per cent. dithizone solution and, finally, with 10 ml of carbon tetrachloride, which removes the residual dithizone and permits the analyst to ascertain that removal of copper has been quantitative. Combine the extracts in a 125-ml conical beaker, and add 4 ml of oxidising acid mixture. Heat gently to remove carbon tetrachloride and then strongly to destroy any remaining organic material. Ensure that the solution is evaporated until fumes are evolved, but do not heat excessively; large variations in the concentration of ammonium salts present cause small errors at low concentrations of copper. Cool to room temperature, add 5 ml each of distilled water and 25 per cent. citric acid solution, adjust the pH to between 8.0 and 9.5 with ammonia solution, sp.gr. 0.880 (see Note), and transfer the solution to a 100-ml calibrated flask. Place the flask in a thermostatically controlled water bath at 20° C, and add 5 ml of 0.5 per cent. *biscyclohexanone oxalyldihydrazone* solution. (A temperature of 20° C was arbitrarily chosen for the dilution of all solutions to a standard volume in order to avoid the difficulties encountered at lower temperatures, e.g., below 15° C formation of the copper complex is sometimes delayed.) Shake the flask, allow the colour to develop for 5 minutes, and dilute to the mark with distilled water at 20° C.

Shake well, and measure the optical density of the solution in a 1-cm cell at 595  $\mu$  with a spectrophotometer that has been set to zero against water. Read the copper content of the alloy from a calibration graph plotted from a range of copper solutions prepared by dilution of the standard copper solution. The most useful range of copper concentration in the final solution is approximately 40 to 200  $\mu$ g per 100 ml.

NOTE—Use wide-range indicator papers in strips of about  $\frac{1}{4}$ -inch to adjust the pH. Carry out a check by placing 1 drop of test solution and 1 drop of  $\alpha$ -naphtholphthalein indicator solution about 0.5 cm apart on a filter-paper. As the drops merge, a distinct blue colour is observed when the pH of the test solution is in the correct range. Any indeterminate colours or colours produced when the spots approach each other but do not merge must be ignored. This procedure was devised to overcome the effects of ammonia evolved from the buffered solutions, which should be stoppered if set aside for any length of time.

TABLE I  
DETERMINATION OF COPPER IN STANDARD ALLOYS

Alloy	Element present	Amount of element present, %	Certified copper content, %	Amount of copper found, %	
<i>Stainless steel—</i>					
B.C.S. No. 235	{ ..	Si	0.82	{ 0.98	{ 0.96, 0.95, 0.99, 0.98, 0.98
		Mn	0.46		
		Ni	8.73		
		Cr	19.01		
		Ti	0.62		
		W	0.68		
<i>Permanent-magnet alloys—</i>					
B.C.S. No. 266	{ ..	Si	0.22	{ 3.33	{ 3.30, 3.32, 3.35, 3.30, 3.35, 3.33, 3.25
		Mn	0.27		
		Ni	13.3		
		Co	23.4		
		Al	7.95		
		Nb	1.21		
B.C.S. No. 233	{ ..	Si	0.57	{ 5.09	{ 5.05, 5.07, 5.12, 5.09, 5.12, 5.03
		Mn	0.235		
		Ni	11.22		
		Co	23.72		
		Al	6.98		
		Ti	0.79		

## RESULTS

To illustrate the precision of the method, recoveries of copper from British Chemical Standard alloys are shown in Table I. A Unicam SP500 spectrophotometer was used to measure the optical densities of the test solutions.

The range of copper concentration covered by the proposed procedure is approximately 2 to 10 per cent., but can be conveniently extended in either direction by varying the sample weight or the aliquot of sample solution and altering the concentrations of the reagents accordingly. The optical density of the final solution can then be controlled so that maximum accuracy is obtained from the scale readings.

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