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# Determination of Copper and Zinc in Brass: Two Basic Methods

Paul-Louis Fabre and Olivier Reynes\*

Université de Toulouse, Université Paul Sabatier, Laboratoire de Génie Chimique, Bat. 2R1, 118 route de Narbonne, F-31062 Toulouse cedex 09, France, and CNRS, Laboratoire de Génie Chimique UMR 5503, F-31062 Toulouse cedex 09, France  
\*reynes@chimie.ups-tlse.fr

Alloys constitute many objects of our daily life and are studied for the development of new materials and the improvement of their properties (1, 2). Because of their particular characteristics (i.e., conductivity, mechanic or corrosion resistances), alloys find applications in many fields such as aeronautics, building, electronics devices, and jewelry. Brass is an alloy of copper and zinc and is familiar to most students. It is an appropriate material for an educational laboratory experiment because of its (i) low cost, (ii) simple composition, mainly copper and zinc (5–45% by mass) and minor elements (<5%), and (iii) ease of dissolution in nitric acid to give  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions. Surprisingly, few pedagogical articles are devoted to the study of brass (3–5), even though in 1927, Stout published a method for the determination of copper in brass (6).

We describe two basic methods for determining the quantity of copper and zinc in brass. This experiment can easily be carried out during a typical 3-h laboratory period in upper-level undergraduate laboratory and does not require advanced instrumentation. The pedagogical interest lies mainly in the basic concepts of analytical chemistry in solutions: oxidative processes according to the standard potentials; selective or successive precipitations according to the solubility products,  $K_{\text{sp}}$ ; potentiometric titrations yielding precipitates; and complexometric titrations with the competition between complexing agents to mask an element.

A brass piece is dissolved in concentrated nitric acid to give  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions; the metals are oxidized by the oxidizing agents ( $\text{H}^+$  and  $\text{NO}_3^-$ ). Students are required to write and justify the redox reactions according to the standard potentials (7). The resulting solution is diluted in a volumetric flask and used in the following titrations as the test solution. The first method is based on acid–base titration of the test solution by sodium hydroxide. The titration shows the three equivalent points corresponding to (i) the neutralization of the excess of nitric acid of the redox reaction; (ii) the complexation of  $\text{Cu}^{2+}$  and the precipitation of  $\text{Cu}(\text{OH})_2$ , the less insoluble hydroxide, and (iii) the complexation of  $\text{Zn}^{2+}$  and the precipitation of  $\text{Zn}(\text{OH})_2$ . Students again write and justify the reactions with the help of the solubility products. Using these reactions and the measured equivalence volumes, they calculate  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations and then the copper and zinc ratio in the brass piece.

The second method consists of two complexometric titrations by EDTA with and without the use of complexing agents for masking the  $\text{Cu}^{2+}$  species. In the first titration, copper and zinc together are titrated by EDTA. In the second titration, sodium thiosulfate is added to complex the  $\text{Cu}^{2+}$  ions and then the titration of  $\text{Zn}^{2+}$  by EDTA is performed. The titration reactions are written and justified by the formation constants of

the complexes. The second titration gives  $[\text{Zn}^{2+}]$ , whereas the first titration gives the sum of  $[\text{Cu}^{2+}]$  and  $[\text{Zn}^{2+}]$ . Once again, the copper and zinc ratios are calculated in the brass piece.

## Experimental Procedure

### Brass Dissolution

Brass pieces, ~770 mg, are reacted in ~5 mL of concentrated nitric acid (70%) in a hood. After complete dissolution of brass, the resulting acid solution is diluted in a 100 mL volumetric flask and used in the following experiments as the test solution.

### Acid–Base Titrations

The test solution (25 mL) is titrated by a sodium hydroxide solution, ~0.1 M. The pH is measured during the addition of NaOH. The pH curve as a function of the volume of NaOH is graphed and shows three jumps. The potentiometric titration is repeated twice.

### Complexometric Titrations

Complexometric titrations are carried out on two buffered solutions prepared by the addition of 10 mL of the test solution to an equal volume of an acetic buffer so that the pH is between 5 and 6. The buffered solutions are titrated with ~0.1 M EDTA solution in presence of xylenol orange as a colored indicator. With the titration of the first buffered solution, the equivalence volume for the titration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  is indicated by the color change from red to green. Before the titration of the second buffered solution, sodium thiosulfate is added to the solution, which complexes selectively the  $\text{Cu}^{2+}$  ions. When the titration is carried out, the color change from red to yellow gives the equivalence volume for the titration  $\text{Zn}^{2+}$ . Each titration is repeated twice.

## Hazards

Sodium hydroxide is caustic and may cause irritation of the eyes and skin. Nitric acid is a strong oxidizer and contact with other material may cause fire. It is a corrosive liquid and may cause severe burns to all body tissue. Dissolution of brass in concentrated nitric acid liberates toxic vapors; the reaction must be carried out in a hood. EDTA and sodium thiosulfate can cause irritation to skin, eyes, and respiratory tract. Students must wear safety glasses, lab coats, and gloves when performing these experiments.

## Results and Discussion

The dissolution of brass in concentrated nitric acid to  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  is observed: the solution turns blue and red-brown vapors escape from the vessel. The red-brown vapors are related to  $\text{NO}_x$  gases evolving from the  $\text{NO}/\text{NO}_3^-$  redox couple; the blue color is attributed to the formation of  $\text{Cu}^{2+}$  cations.

The determination of the  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations is achieved by acid–base titration through the successive precipitations of the hydroxides  $\text{Cu}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$ . Titration of the test solution by sodium hydroxide  $\text{NaOH}$  is represented by a curve, pH versus  $\text{NaOH}$  volume, that gives the evidence of three neutralization reactions by three pH jumps. The first jump is related to the remaining nitric acid (strong acid) and the second jump is attributed to the precipitation of copper hydroxide  $\text{Cu}(\text{OH})_2$  whose solubility product ( $K_{\text{sp}1} = 2 \times 10^{-20}$ ) is lower than the solubility product ( $K_{\text{sp}2} = 3 \times 10^{-17}$ ) of zinc hydroxide  $\text{Zn}(\text{OH})_2$ . The blue precipitate is characteristic of the  $\text{Cu}(\text{OH})_2$  formation. The third jump is attributed to the precipitation of zinc hydroxide  $\text{Zn}(\text{OH})_2$  and a white precipitate appears. Taking into account the different solubility products,  $K_{\text{sp}}$ , the student analyzes the neutralization curve and calculates the beginning pH of the precipitations. The equivalence volumes for the second and third pH jumps allow the calculation of the concentrations of copper and zinc cations. Then, the relative mass of copper and zinc in the analyzed brass pieces are obtained by considering the initial volume of the test solution and the mass of brass dissolved.

The second method for brass analysis consists in complexometric titrations by EDTA, which is an efficient complexing agent of metallic cations (8). Xylenol orange is used as a colored indicator for the detection of equivalence point (volume). The analysis is carried out via two titrations. In the first titration, the total concentration of cations  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  is ascertained as the complexation constants of  $\text{Cu}$ –EDTA ( $\log \beta_1 = 18.8$ ) and  $\text{Zn}$ –EDTA ( $\log \beta_2 = 16.5$ ) are similar (8) and the complexes are formed simultaneously. In the second titration, the addition of sodium thiosulfate masks the copper cation. According to the complexation constants,  $\beta_1' = 10^{10.3}$  for copper and  $\beta_2' = 10^{2.3}$  for zinc (9), the complexation of  $\text{Cu}^{2+}$  is selective and  $\text{Cu}^{2+}$  is masked. Thus, titration of this solution by EDTA is restricted to  $\text{Zn}^{2+}$  cations. Taking into account the two titrations, concentrations of copper and zinc are determined.

Comparing the results of the two methods, it appears that the complexometric titrations give the best results when compared to fluorescence X-ray analysis (see the supporting information). The potentiometric titration results were significantly different from those obtained by complexometric and fluorescence X-ray analysis. The difference observed between complexometric and potentiometric titrations can be explained by the approximations used in the

mass balance equation. During addition of sodium hydroxide, a basic cupric complex (10) and the soluble  $[\text{Zn}(\text{OH})_2]^{4-}$  can be formed and were not considered here.

## Conclusion

This educative laboratory experiment is easily carried out in a 3-h period, without advanced instrumentation. The experiment uses a protocol similar to those of standard laboratory: sample preparation, dilution, method, analysis, and results. Each step must be rigorously performed. From an academic point of view, this experiment illustrates the basic concepts of solution chemistry. The oxidative dissolution of brass pieces relates to the standard potentials of the redox couples. The potentiometric titrations yield precipitates that imply selective or successive precipitations according to the solubility products  $K_{\text{sp}}$ . Considering the apparent constants according to Ringbom (11), the complexometric titrations with the competition between complexing agents to mask an element could be the object of a further study.

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