Utilization of Ball Pen Refill Nozzle for Developing a New Experiment

Sudesh Bhaskar Ghoderao
Associate Professor
RNC Arts, JDB Commerce and NSC Science College, Nashik Road, Nashik, India

Abstract: The most common writing material - ball pen - a stationary, consumer product many times has a replaceable writing unit – a nozzle with refill. After the ink is consumed, the refill is thrown away with nozzle as a waste material. But in reality it is found that the brass material of the nozzle socket of used-up refill is a useful material for experimental work. It can be used by the students for complete- or single constituent - analysis. In the present paper, a single constituent of brass, copper is determined. The used-up ball pen refill sockets or tips may also serve as a source of brass material.

IndexTerms **- Chemistry Education, Pedagogy, Low Cost Experiment, Determination of Copper, Ball pen refill**

I. INTRODUCTION

In our day-to-day life we come across the most common writing material - ball (point) pen - a consumer product. It usually consists of a replaceable writing unit - a ball pen refill, and a holder for it **[1]**. (In some models of ball pen (jotter pens) the holder itself is the writing unit and it is discarded after the ink is used up). In all cases the writing unit (commonly known as "refill") consists of an ink reservoir (containing viscous ink) and the front tip portion. The metal tip has a socket that contains a ball at the point portion. The tip of the socket is constructed such that the ball cannot fall out yet can rotate freely when in contact with writing surface. The inner construction of socket is such that the ball is constantly bathed in ink from the reservoir. This ball easily transfers the viscous ink from the reservoir onto the writing surface as it rotates. Early models of ballpoint pen in use had a stainless steel ball and brass housing **[2].** Today although the ball pens are made of many materials including materials as various polymeric or of metallic parts as those of steel, brass, bronze and other copper alloys, the commonly available now-a-days refills have plastic tube as an ink reservoir fitted to a brass tip portion or nozzle containing the ball of stainless steel at the point (that touches the writing surface). The solvents used in ink-preparation are either glycols or mixtures of aromatic alcohols and polyhydric ethers. Additives include wetting agents (to improve coverage on the paper) and organic acids (to increase intensity of the color) **[2].** After the ink is consumed, the refill is thrown away as a waste material. But in reality it is found that such used-up refill is a useful material for teaching aids and experimental work. The brass material of its nozzle socket can be used by the students for complete- or single constituent - analysis. In the present work, a single constituent of brass, copper is determined. About six such samples of ball pen refills of different types as ordinary, giant-size, jotter etc. manufactured by different companies were analyzed for copper content. The used-up ball refill sockets or tips may also serve as a source of brass material.

II. THEORETICAL BACKGROUND

Isolation of sample

After removing the plastic tube and the ball from socket, the removal of ink in inner part of the brass nozzle of ball pen refill is done. For this thorough cleaning is done with glacial acetic acid, as the ink dissolves in glacial acetic acid easily as compared to that in aliphatic alcohol or in any other organic solvent **[1,2]**. After this the repeated washing with distilled water is done to remove traces of acid. Lastly washing with methanol is done to remove the traces of water, as water is miscible with methanol. The nozzle is dried at room temperature to allow the removal of organic solvent (methanol) by evaporation.

Disintegration of Sample

The important constituents of brass are copper (50-90 %), Zn (20-40 %), Sn (0-6 %), Pb (0-2 %) and Fe (0-1 %). The analysis involves the separation and masking processes for other constituents in the determination of copper. The sample is treated with hot nitric acid (6 M) in preference to other acids. Here, zinc dissolves easily (evolving hydrogen) but copper being less electro-positive requires this oxidizing acid (which gives nitrogen dioxide). There is also precipitation of metastannic acid or tin oxide ($SnO_2.H_2O$) from traces of tin. The treatment with concentrated sulphuric acid is the second step in which lead (in traces) forms insoluble lead sulphate while excess of nitric acid is decomposed by heating till brown fumes of nitrogen dioxide cease and white fumes of sulphur trioxide start evolving (indicating expulsion of HNO_3). For iodometry (used for estimating copper) the solution should be free from oxides of nitrogen because potassium iodide reacts with them. Their removal is done by heating the solution in presence of concentrated sulphuric acid. The insoluble materials can be separated after the dilution of the solution by filtration. The filtrate and the washings of the residue may be mixed and diluted to known volume exactly and an aliquot from this solution can be used for the determination of copper.

Iodometric determination of copper

Strong reducing agents such as sodium thiosulphate react completely and rapidly with iodine even in acidic medium **[3,4**]. If a strong oxidizing agent (such as Cu(II)) to be determined is treated in neutral or acidic solution with a large excess of iodide ion , the later reacts as a reducing agent and the oxidant will be quantitatively reduced. In such cases, an equivalent amount of iodine is liberated and is then titrated with a standard solution of sodium thiosulphate (reducing agent) by using starch as an indicator. Starch reacts with iodine in the presence of iodide to form an intensely blue colored complex which is visible at very low concentrations of iodine.

In iodometric determination of copper, Cu^{2+} is converted to Cu^{+} by I^{-} and amount of iodine (I_2) equivalent to Cu^{2+} is liberated. It is estimated titrimetrically using the previously standardized solution of $S_2O_3^{2-}$ and the following relationship.

Equivalent for titrimetry: $(Na_2S_2O_3)\ /2 = (I_2)\ /2 = (Cu_2I_2)\ /\ 2 = (KI)\ /1 = (Cu)\ /1$

The addition of small amount of SCN^{-} is done at the end of titration to get the end point rapidly (thus avoiding appreciable reduction of iodine by thiocyanate). It removes the difficulty of detecting the end point in presence of Cu_2I_2 alone. The later is not pure white owing to adsorbed iodine **[5]**. The cuprous iodide formed is converted to less soluble cuprous thiocyanate which has less

tendency to adsorb iodine (at least on surface layers) and is, therefore, nearly white **[6]**. The persistence of white color (of the precipitate) for 15 seconds is the end point of titration.

Standardization of sodium thiosulphate is done using standard $K_2Cr_2O_7$, solution. Potassium dichromate is reduced by potassium iodide in acidic medium to form a green chromic salt, and an equivalent amount of iodine is set free. This liberated iodine is titrated against sodium thiosulphate using starch as an indicator.

For calculating exact normality of $Na_2S_2O_3$ following relation is useful.

Equivalent for titrimetry: $(Na_2S_2O_3) / 2 = (I_2) / 2 = (KI) /1 = (K_2Cr_2O_7) / 6$

As the pH of the solution for iodometric titration required is approx. 3. The removal of strong acids is done by boiling the solution as much as possible and then the pH is adjusted using dilute ammonia followed by adding the amount of H_2SO_4 and H_3PO_4 just adequate for the system. The role of phosphoric acid (85 %) is to mask the iron impurities in brass. (It is desirable to use sodium bicarbonate to neutralize acids and then acetic acid to adjust the pH) **[4,7]**.

III. EXPERIMENTAL

Reagents

Disintegration of sample

Nitric acid (6 M): 37.5 mL HNO_3 (conc.) is diluted to l00 mL

Sulphuric acid (conc.)

Determination of Cu^{2+}

Ammonia (1:1)

Sulphuric acid (9 M): 17 mL H_2SO_4 (conc.) mixed cautiously with water to get finally 100 mL solution.

Phosphoric acid (85 %): Syrupy or concentrated ortho-phosphoric acid is used here directly

Potassium Iodide solution (10 %): 10 g KI dissolved and made to 100 mL.

Sodium thiosulphate solution (0.025 N approx.): 6.25 g $Na_2S_2O_3.5H_2O$ dissolved in water and diluted to 1 L.

Starch solution (1 %)(freshly prepared) : The paste in water of about 1 g of soluble starch is poured with constant stirring to ~ 100 mL of boiling distilled water. The solution is boiled for l minute, cooled and in it is dissolved - 2 g of KI.

Ammonium thiocyanate solution (10 %): 10 g of NH_4SCN dissolved to get 100 mL solution.

Potassium dichromate (standard solution) (0.025 N): 1.225 g of $K_2Cr_2O_7$ is dissolved in water and diluted to 1 L exactly.

Disintegration of sample

The accurately weighed sample i.e. a nozzle (It is 0.2- 0.3 g generally) is transferred to a 100 mL conical flask. To it is added ~ 4 mL of nitric acid (6 M). It is warmed carefully after putting a stem-cut funnel on it; until the sample dissolves completely. It is cooled and then to it is added ~ 6 mL of concentrated sulphuric acid. The contents of flask are heated until dense white fumes of sulphur trioxide are given out. The contents are allowed to cool and then diluted to ~ 20 mL. The solution is then filtered through Whatman No. 42 filter paper to remove any insoluble material in the solution. The residue, if any, is washed repeatedly with hot water till free from acid. This residue is rejected. The filtrate and washings are mixed together, cooled to room temperature and diluted to a known volume, here 250 mL, exactly. This solution is used for the determination of copper.

Iodometric determination of copper

Standardization of $Na_2S_2O_3$ (0.025 N approx.)

An aliquot of 25 mL of potassium dichromate solution (0.025 N) is mixed with 20 mL of hydrochloric acid solution (1:1) and 20 mL of freshly prepared potassium iodide solution (10%). The liberated iodine is titrated immediately against sodium thiosulphate solution (approx. 0.025 N) using starch as an indicator. The end point is disappearance of blue color and development of pale green colour (of Cr^{3+}). In the present experiment for 25 mL of $K_2Cr_2O_7$ (0.025 N) the mean titration reading = 27.7 mL of $Na_2S_2O_3$.

Exact normality of $Na_2S_2O_3$ = 0.02252

Determination of copper [4]

An aliquot of 25 mL of the diluted solution is pipetted out in a 250 mL conical flask. It is neutralized by drop wise addition of ammonia (1:1) with constant stirring until faint permanent light blue precipitate of cupric hydroxide ($Cu(OH)_2$) forms. (In case the solution becomes deep blue due to formation of $[Cu(NH_3)_4]^{+2}$, the ammonia is boiled off). Then is added sulphuric acid (3 M) a drop at a time with stirring till the precipitate dissolves. Followed by this is added ~ 2 mL of orthophosphoric acid (85 %) and 10 mL of potassium iodide (freshly prepared 10 %). The contents of flask are immediately titrated against previously standardized sodium thiosulphate (0.02252N) till the brownish solution becomes pale yellow. To it ~ 2 mL of freshly prepared starch (1 %) indicator is added and the titration is continued until the blue color becomes faint. To this solution, 5 mL of NH_4SCN (10%) is added and the solution swirled for 30 seconds. The titration is completed when the first disappearance of blue color of starch iodine takes place and persists for at least 15 seconds.

IV. RESULTS AND DISCUSSION

The details for analysis of a representative sample R1 is given in the following information and the results for all the samples are given in Table 1.

Sample: Ball pen refill R1

Weight of the clean brass nozzle tip taken for analysis = 0.17802 g

Determination of Cu^{2+}

Mean titration reading = 7.3 mL of $Na_2S_2O_3$(0.02252 N)

1 mL of 1 N $Na_2S_2O_3$ = 63.54 mg Cu^{2+}

7.3 mL of 0.02252 N $Na_2S_2O_3$ = 10.44 mg Cu^{2+} (in 25 mL aliquot)

Amount of Cu^{2+} in 250 mL original solution containing disintegrated sample = 104.4 mg.

Amount of Cu^{2+} present in 0.17802 g of brass = 0.10440 g

Percentage of copper in the brass sample = 58.64

Table 1: Estimation of copper from brass socket of used-up ball pen refill

Code Number and other information about sample	Sample (g)	Titer, mL $Na_2S_2O_3$ (0.02252 N)	Calculated % Cu	Average % Cu
R1 (brass tip for red ink)	0.17802	7.3	58.64	58.56
	0.17128	7.0	58.48	
R2 (brass tip for blue ink)	0.21940	8.9	58.02	57.84
	0.21835	8.8	57.66	
R3 (brass tip for blue ink)	0.17461	7.1	58.18	58.41
	0.16348	6.7	58.64	
R4 (lustrous white tip for blue ink)	0.25080	10.2	58.19	58.20
	0.24820	10.1	58.22	
R5 (lustrous white tip for red ink)	0.23740	9.7	58.46	58.29
	0.22890	9.3	58.13	
R6 (lustrous white tip for red ink)	0.22750	9.4	59.12	58.92
	0.23150	9.5	58.72	

IV. CONCLUSION

The material used for this experiment is used-up and so its utilization instead of that of brass turnings is economically favorable. The disintegration of the sample is rapid one, since the nozzle is made up of thin sheet of brass. The analysis of brass-nozzle of ball pan refill for copper is studied here. One can extend it for the estimation of zinc also which can be done by complexometric method after removing copper from the aliquot.

For zinc-estimation by gravimetric method (pyrophosphate method), however, it will be preferable to disintegrate two nozzles to get the disintegrated solution with concentration of zinc suitable for analysis. All the results given in Table 1 indicate that brass used in the manufacture of refi1l nozzle is similar to the commonly seen composition of brass.

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