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Environmentally benign Iodometric method for estimation of copper

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ABSTRACT

Copper is one of the most important metals as it is used in alloys as well as electric and electronic industry. The composition of alloy strongly affects its properties. Instrumental methods are preferred for quickly finding composition of alloys. However, the main limitations in these methods are high cost of instruments and need for skilled supervision for maintenance & operations. To overcome limitations of instrumental analysis, to reduce the sample size and to reduce waste, a novel eco-friendly micro-titration method based on counting of number of drops is reported. Students learn chemical quantitative analysis and practice iodometry in their lab courses for estimation of copper. The green method was used along with conventional iodometry for training of first year UG students. The data of estimated copper using the two methods were collected and analyzed. Statistical comparison of the results of these methods shows fairly good agreement and indicates no significant difference in precision and accuracy. The novel method is more environmentally benign as it helps in energy savings, a drastic reduction of reagent consumption, and less waste generation.

Keywords: Green analytical Chemistry, Iodometry, Copper

INTRODUCTION

Copper is one of the most important metals for materials as well as biological applications.[1] It has very good electric and thermal conductivity.[2] It is used in electric & electronic industry and for making alloys with tin (known as bronzes), zinc (known as brasses), silver (used for jewellery), nickel (used for coins)[3] etc. The composition of alloy strongly affects its chemical resistivity and mechanical properties.[4,5] Thus, the ability to determine alloy composition is important branch of chemical quantitative analysis.[5] The well known method for the iodometric determination of copper was introduced by De Haen in 1854. The details of this method were studied by Gooch and Heath.[7] This method is based upon the reversible reaction: $Cu^{2+} + 2I^- \leftrightarrow Cu^+ + I^- + ½ I_2$. This reversible reaction had been shown by Bray and Mackay[8] to obey the mass law within certain limits in dilute solutions. Shaffer and Hartmann[9] reported that the potassium iodide must be added to give a final concentration of about 4 to 5 gm per 100 mL of solution for the determination of cupric salts. For the determination of copper (II), the conventional iodometric method requires the addition of just enough potassium iodide to form solid copper (I) iodide and to maintain the liberated iodine in solution. The direct titration of this mixture with standard thiosulfate leads to inaccurate results, because of the adsorption of iodine on precipitate, which becomes violet or brownish in color thus leading to obscure the end point. To overcome this difficulty, a small excess of ammonium thiocyanate (or potassium thiocyanate) is added just before the end point. This reacts at the surface of the copper (I) iodide to form the less soluble copper (I) thiocyanate. The previously adsorbed iodine is released into the solution because the copper (I) thiocyanate has much less affinity for triiodide ion. As a consequence, the intensity of the color of the precipitate is considerably reduced, so that the end point can be more easily located.[10,11]

Sustainability aims for improving the quality of human life within the carrying capacity of supporting ecosystems. It is possible to achieve, provided we all leave the world better than we found it, take no more than we need, try not to harm life or the environment, make changes for the improvement, and stop separating humanity from nature, and truth from morality.[12-14] For improvements in the quality of chemical analyses, apart from development in instrumentation and methodologies, efforts are being made to reduce the negative impact of chemical analyses on the environment and to enable implementation of sustainable development

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principals to analytical laboratories. The most important challenge to the future of Green Analytical Chemistry is to reach a compromise between the increasing quality of results and the improving environmental friendliness of analytical methods. Namiesnik et al.[15] proposed the mnemonic "SIGNIFICANCE" for green analytical practices.

S: Select direct analytical technique
I: Integrate analytical processes and operations
G: Generate as little waste as possible and treat it properly
N: Never waste energy
I: Implement automation and miniaturization of methods
F: Favor reagents obtained from renewable source
I: Increase safety for operator
C: Carry out in-situ measurements
A: Avoid derivatization
N: Note that the sample number and size should be minimal
C: Choose multi-analyte or multi-parameter method
E: Eliminate or replace toxic reagents

Instrumental methods involve the use of standard instruments. The appropriate uses of these instruments either require separation, extraction or masking of elements from other interfering elements. Further, several instrumental parameters must be controlled. Generally, the cost of the instrument is very high so due to financial constraints instruments are not available at most school, colleges and quality control laboratories in developing and underdeveloped nations. Conventional titrimetry is still widely used in analytical chemistry because of its simplicity and low cost with little sacrifice in precision and accuracy.[15] Despite much discussion, however, there is scope in existing practices for improvements in safety, eco-friendliness, time requirements and cost reductions.

Research questions:

How can students find copper by employing fewer quantities of sodium thiosulphate and other reagents? Will the proposed method be safe, cost-effective, simple, accurate, and fast?

EXPERIMENTAL

APPARATUS

Calibrated glass wares like conical flask, measuring cylinder, pipettes supplied by Borosil Glass Works Ltd India were used.

REAGENTS

All chemicals used were of laboratory reagent grade. Distilled water was used for making the solutions. The Copper sulphate pentahydrate, $CuSO_4.5H_2O$ (assay 98.5%), sodium thiosulphate, $Na_2S_2O_3$ (assay 99%), acetic acid (assay 99%), sodium carbonate (assay 99.5%) supplied by Qualikems Laboratory Reagent, Qualikems Fine Chemicals Pvt. Ltd, India were used. Starch supplied by Fischer Scientific, Qualigens Fine Chemicals, India was used. Potassium iodide, KI, (assay 99%), supplied by Rankem, RFCL limited was used. Ammonium thiocyanate (assay 98%), CDH laboratory reagent was used.

SOLUTIONS

$CuSO_4.5H_2O$ Solution

Weighed about 0.31 g and 0.62 g of $CuSO_4.5H_2O$ crystals and transferred them to 250 mL measuring flasks. Added some distilled water and 5 mL of dil. acetic acid in both the flasks. Dissolve the $CuSO_4.5H_2O$ and made the solutions to 250 mL.[11]

$Na_2S_2O_3$ Solution, 0.01N & 0.005 N

0.01N & 0.005 N $Na_2S_2O_3$ Solution were prepared by dissolving 2.48 g and 1.24 g $Na_2S_2O_3$ respectively in distilled water and diluted to 1L. The sodium thiosulphate solutions were standardized with the help of $CuSO_4$ solution.[16]

Starch indicator solution

A paste of 1 g of starch was made in water. 100 mL of boiling water was gradually added with constant stirring. Boiled for a minute & then cooled before use.

PROCEDURE

Conventional Titrimetry (Method A: Macroscale)

2 ml of the $CuSO_4$ solution was placed in clean 10 ml conical flask. To this was added sodium carbonate solution drop by drop till a faint permanent precipitate remained even on shaking. Then dil. acetic acid was added dropwise until the precipate dissolved. 5 mg of solid KI was added to it and allowed the mixture to stand for 3 to 5 minutes in the dark. The solution turned brown. This was titrated against 0.005 (or 0.01) N sodium thiosulphate solution until there was color change from brown to yellow. Two drops of starch indicator was added along with 1 drop of ammonium thiocyanate solution. The solution turned blue. Sodium thiosulphate solution was further added till the blue color of the solution disappeared. The titer value was noted down. The procedure was repeated 4-5 times and calculations were done with either concordant or the average value. The amount of copper in the measured aliquot was calculated by using the following equation:

Strength of Cu^{2+} (g/L) = $y = 63.5(N_2V_2/V_1)$ (1)
Cu^{2+} (%) in $CuSO_4.5H_2O$ crystals = 100 y/strength of $CuSO_4.5H_2O$ crystals (2)
Where N_2 = Normal concentration of sodium thiosulphate solution, V_2 = Volume of sodium thiosulphate solution, mL, and V_1 is the volume of $CuSO_4$ solution taken, mL.[11]

GREEN APPROACHES (METHOD B1 AND B2: MICROSCALE)

Green approach using pasture pipettes is described in this section.

Calibration of pasture pipette

Measuring cylinder was used to collect number of drops formed by $CuSO_4$ solution using pasture pipette. Reverse of number of drops in 1 mL formed by $CuSO_4$ solution given average volume of 1 drop of this solution. Similarly, average

volume of 1 drop of sodium thiosulphate solution was also determined with the help of separate pasture pipette.

Titration by Drop Counting

GREEN APPROACH B1

10 drops of the $CuSO_4$ solution was placed in clean 10 ml conical flask. To this was added sodium carbonate solution drop by drop till a faint permanent precipitate remained even on shaking. Then dil. acetic acid was added drop wise until the precipitate dissolved. 1 mg of solid KI was added to it and allowed the mixture to stand for 3 to 5 minutes in the dark. The solution turned brown. This was titrated against 0.005 (or 0.01) N sodium thiosulphate solution until there was color change from brown to yellow. One drop of starch indicator was added along with 1 drop of ammonium thiocyanate solution. The solution turned blue. Sodium thiosulphate solution was further added till the blue color of the solution disappeared. The titer value was noted down. The procedure was repeated 4-5 times.

The concordant or average number of drops of sodium thiosulphate solution consumed was multiplied with the average volume per drop to calculate volume of sodium thiosulphate solution. The average volume per drop of $CuSO_4$ solution was multiplied with 10 to calculate volume of $CuSO_4$ solution.
The calculation was done by using the equations 1 and 2 described earlier.

GREEN APPROACH B2

The first observation was taken as per the method described above in Green approach "B1". For the second and subsequent observations, the titrations were continued in the same conical flask one after the other without discarding anything. Only 10 drops of $CuSO_4$ solution were added in a conical flask, the starch indicator and ammonium thiocyanate were not added again as they were already present. The amount of copper in the measured aliquot was calculated by using the equation (1) described earlier.

Statistical Sampling

Each student was directed to take 3-5 observations. 20 students were included in one batch. Four such batches (each having 20 students) were made and they repeated experiment on different timings. More than 400 samples were tested by different methods. From the reported results for these samples values of average and percentage error were calculated. ***Accuracy*** is how close a measured value is to the reference (actual or true) value. The absolute error is the difference between the experimentally determined and the true values of concentration of copper sulphate. The relative error is the absolute error divided by the true value. The accuracy was determined as the percentage relative error between the measured and taken concentrations. ***Precision*** is how close the measured values are to each other. The repeatability of the proposed method was determined by performing replicate determinations.[17]

Table 1: Stepwise Procedure & Explanations of Iodometric estimation of Copper sulphate

Procedure	**Observation**	**Requirements & Explanations**
Pipette out 2 mL (or take 10 drops) of copper sulphate solution in a conical flask and neutralize the solution by drop wise addition of sodium carbonate solution.	Faint precipitate of $Cu_2(OH)_2CO_3$ get formed.	Iodometric titration fails when any mineral acid is present in the solution. Therefore, it must be neutralized before starting the titration.
Add few drops of dil. acetic acid.	Precipitate dissolves	Iodine reacts with alkali's to form hypoiodide ion (IO^-) which is stronger oxidizing agent than I_2. Hypoiodide ion partly oxidizes thiosulphate to sulphate. Thus, pH of solution should not be greater than 9.
Add 5 mg of KI in the conical flask, cover its mouth with watch glass, keep the flask in cool and dark place, wait for 3-5 minutes	Solution turns brown due to liberated iodine.	Solubility of I_2 in water (0.00134 mol/L at 25˚C) is low. The liberated iodine then dissolves in excess KI forming the triiodide complex, KI_3, which slowly releases I_2 during titration; In the presence of sunlight, oxygen of air oxidizes iodide to iodine in strong acid solution as per following equation: $O_2 + 4\ H^+ + 4I^- \rightarrow 2\ I_2 + 2\ H_20$ Iodine is volatile so titration is carried out in cold; The reaction between $CuSO_4$ & KI is slow so solution is allowed to stand for 5 minutes. $2\ CuSO_4.5H_2O + 4\ KI \rightarrow 2CuI_2 + 2K_2SO_4 + 5H_2O$ $2CuI_2 \rightarrow I_2 + Cu_2I_2$
Titrate the liberated iodine with standard sodium thiosulphate solution by addition of x mL from burette or x drops from beral pipette.	Solution turns light yellow.	This fading of color is due to consumption of I_2 on its reaction with thiosulphate solution as per the following equation: $I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ NaI$
When the color of the solution fades to a light yellow, add 1 or 2 drops of starch.	Solution turns deep blue.	The amylase fraction (20% water soluble part) gives red color with I_2 and amylopectin (80%

		water insoluble part) gives black color with I_2 due the formation of complex. As a whole, starch gives intense blue (violet) color with I_2. Starch is never added in the beginning of titration because it will be a permanent deep blue complex which does not disappear even after the addition of a large quantity of sodium thiosulphate. Thus, correct detection of end point becomes difficult. Moreover, in acidic solutions, when concentration of iodine is high, starch tends to undergo decomposition. Therefore, addition of starch is delayed until near the equivalence point of the titration. Starch is easily biodegraded. A hydrolysis product of starch is glucose, which is a reducing agent. A partly hydrolyzed solution of starch could thus be a source of error in a titration.
Continue titration with sodium thiosulphate solution. Add small amount of ammonium thiocyanate towards the end of titration. Add more hypo solution (y mL from burette or y drops from beral pipette) till the end point is observed.	Blue color discharges and a white residue are left in the flask.	A large amount of cuprous iodide (Cu_2I_2) is precipitated towards the end of the titration. The estimation of copper is complicated by the absorption of iodine over cuprous iodide precipitated and its very slow release there from. To overcome this, a small amount of ammonium thiocyanate is added when the blue color begins to fade to displace the absorbed iodine from (Cu_2I_2) precipitate; the blue color will instantly become more intense. For calculations, use total volume of hypo solution (x+y) mL.

Table 2: Table of frequency versus volume of Sodium thiosulphate (0.005 N) solution required for titration of 4 mL Copper sulphate solution by conventional method

.No.	*Volume of Sodium thiosulphate (0.005 N) solution required for titration of 4 mL Copper sulphate solution by conventional method*	*Frequency (= No. of students who reported same volume)*
1	3.5	5
2	3.6	4
3	3.7	12
4	3.8	18
5	3.9	10
6	4	12
7	4.1	6
8	4.2	0
9	4.3	2
Total	35.1	69
	Average volume of Sodium thiosulphate (0.005 N) solution required for titration of 4 mL Copper sulphate solution by conventional method	3.84 mL

Table 3: Table of frequency versus volume of Sodium thiosulphate (0.01 N) solution required for titration of 4 mL Copper sulphate solution by conventional method

S.No.	*Volume of Sodium thiosulphate (0.01 N) solution required for titration of 4 mL Copper sulphate solution by conventional method*	*Frequency (= No. of students who reported same volume)*
1	1.6	2
2	1.7	6
3	1.8	15
4	1.9	14
5	2	20
6	2.1	3
7	2.2	1
8	2.3	1
Total	15.6	62
	Average volume of Sodium thiosulphate (0.01 N) solution required for titration of 4 mL Copper sulphate solution by conventional method	1.9 mL

Table 4: Table of frequency versus number of drops in 1 mL Sodium thiosulphate (0.01 N) solution

S.No.	*Number of drops in 1 mL Sodium thiosulphate (0.01 N) solution*	*Frequency (= No. of students who reported result)*
1	14	1
2	15	4
3	16	5
4	17	8
5	18	5
6	19	3
7	20	8
Total		38
	Average number of drops in 1 mL sodium thiosulphate solution	17.56

Table 5: Table of frequency versus number of drops in 1 mL of copper sulphate solution

S.No.	*Number of drops in 1 mL of copper sulphate solution*	*Frequency (= No. of students who reported result)*
1	14	1
2	15	9
3	16	8
4	17	5
5	18	3
6	19	2
7	20	3
8	21	2
9	22	1
Total		34
	Average number of drops in 1 mL sodium thiosulphate solution	17

Table 6: Comparison of results obtained for conventional & Environmentally benign methods of estimation of copper by iodometry

S.No.	*Method*	*$CuSO_4$ taken (g/L)*	*Sodium thiosulphate used*	*$CuSO_4$ (mean) experimentally determined (g/L)*	*Relative Error (%)*
1	Conventional method with starch indicator reused	25.5	0.01 N	24.23	5.00
2	Green method with starch indicator reused	25.5	0.01 N	24.44	4.16
3	Conventional method with starch indicator discarded	25.5	0.005 N	24.49	3.95
4	Green method with starch indicator discarded	25.5	0.005 N	25.18	1.26

RESULTS AND DISCUSSIONS

Accuracy and Precision

The results of this study are compiled in Tables 2-6 and shown in Figures 1-5. The modes are the values at the points around which the items tend to be most heavily concentrated in a distribution. The values of volumes 3.8 mL and 4.0 mL (the variables) are the values having the maximum frequency in a data of Table 2. These two values are major and minor modes in a distribution. The titrimetric end point results obtained for a large number (69) of replicate readings were found to be distributed about the mean in a roughly unsymmetrical manner as shown in Figure 1. Random (indeterminate) errors manifest themselves by the slight

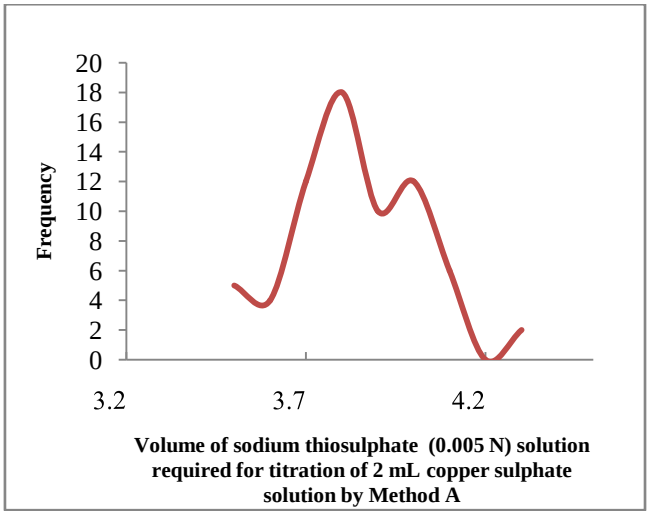

Figure 1: Plot of of frequency versus volume of Sodium thiosulphate (0.005 N) solution required for titration of 4 mL Copper sulphate solution by conventional method

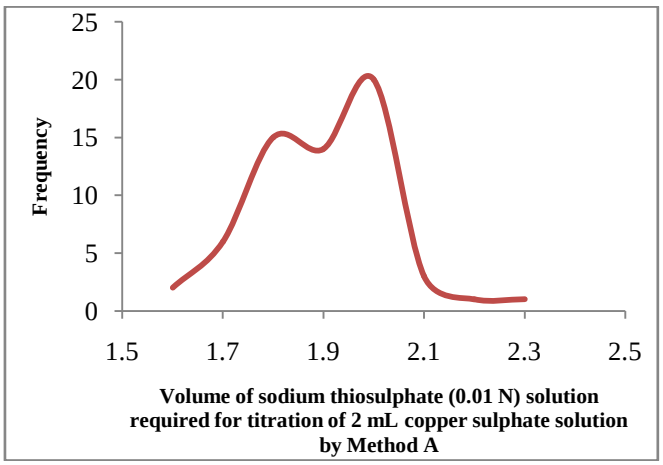

Figure 2: Plot of frequency versus volume of Sodium thiosulphate (0.01 N) solution required for titration of 4 mL Copper sulphate solution by conventional method

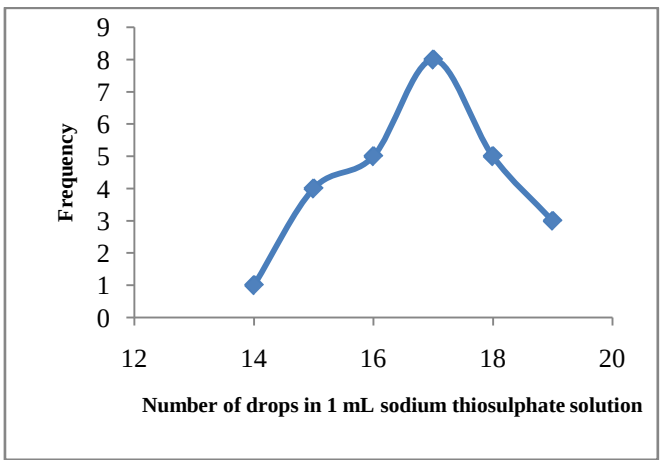

Figure 3: Plot of frequency versus number of drops in 1 mL Sodium thiosulphate (0.01 N) solution

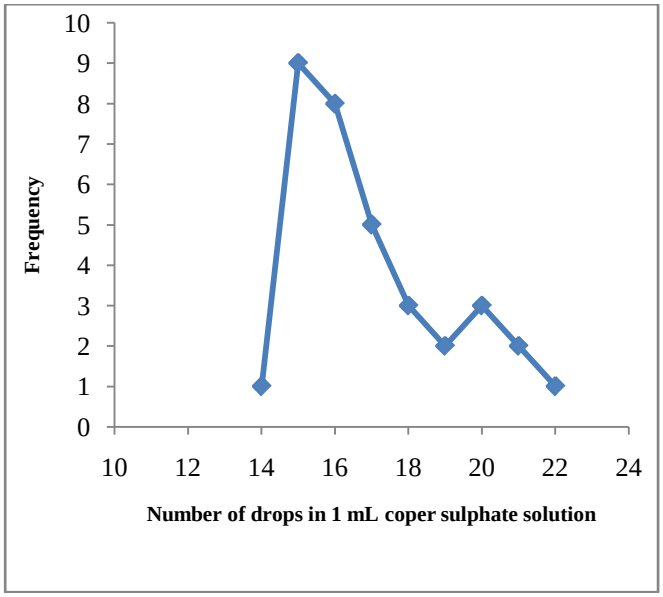

Figure 4: Plot of of frequency versus number of drops in 1 mL of copper sulphate solution

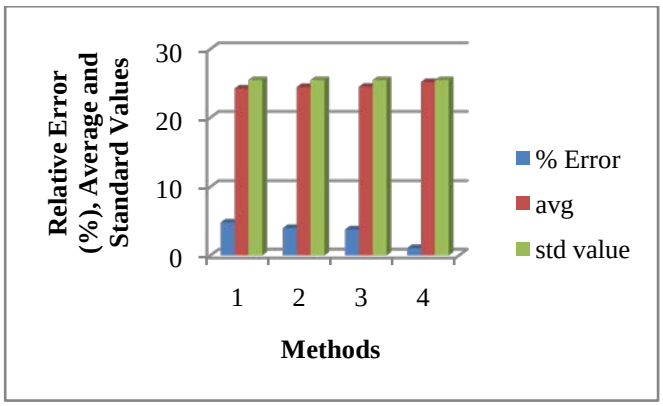

Figure 5: The Standard value, average value and Error (%) value for conventional titrimetric (1 & 3) and green approaches (2 & 4). Note the reduction of Relative Error (%) value of green approach 4 as compared to other methods. The green approach needed only 10% of the time, saved ≥ 90% cost of the chemicals and is safe.

variations that occur in successive measurements made by the same student with the greatest care under nearly identical conditions. The random errors from titration processes in Figure 1 and Figure 2 could be described by bimodal bell curves. The distributions are spread unsymmetrically around major and minor modes. The figure is not a normal distribution plot because there is no "common cause" variation when different students carry out the same titration.

Furthermore, as the outcome of two different distributions (viz. the random error associated with replicate measurements, and the variation that may arise between the individual students) are combined in one set of data, so a double-peaked or bimodal distribution plot is obtained. The mode is the value of the volume at which the curve reaches its peak or maximum. In a bimodal distribution, we observe two maximum points, which state that these points are higher than the neighboring values in terms of frequencies with which they are observed. The mode values were not used in statistical analysis, as they are not algebraically defined and the fluctuation in the frequency of observation is dependent on the sample size.[13,14] As random errors and the scatter in the data are high so the probability distribution would not be close to a normal distribution. The Figure 3 describes the skewed distribution in real-titration processes reasonably well. The results of Tables 4 & 5 and Figures 3 & 4 can be explained on the basis of the Central Limit Theorem (Due to Laplace), according to which, when number of drops formed from a definite volume (random variables, "n") are added together, the distribution of the sum tends towards the normal as "n" increases. The relative errors (%) in the titrations (Table 6) are much larger. These are due to student's unfamiliarity with the titrations, variations in the stage at which different students add starch indicator, errors in judging the end point, etc. Some error may also result from the addition of thiocyanate even near the end point because triiodide ion is known to oxidize thiocyanate slowly.[10,16,18,19]

The validity of the green approach needed comparison of the obtained results with those of conventional method.

Procedure validity and comparative studies

The green approach (4) proved to be reproducible and precise. This is apparent from Table 5 and Figure 5. More precise and accurate results are obtained from this method since no stringent conditions to be maintained. The green methods utilize easily available reagents in 10-20 times smaller quantities which demonstrates cost-effectiveness. This work has extended the scope of environmentally friendly methods used for the training of first year UG students.[16,20]

Implications for research and for chemistry learning: The green approaches discussed in this manuscript can be used for training of the students in laboratories of schools and colleges. As lots of time is saved during actual performance so more time can be allotted to teachers for explaining the theory behind the experiment. For instance, we were able to discuss the detailed background of this experiment (Table 1) in the same time slot of lab.

Limitations: Each drop needs to be carefully added and counted otherwise results obtained will have errors.

CONCLUSION

This article concerns with the investigation of a green approach for iodometric estimation of copper. Statistical comparison of the results with a conventional titration method provided evidence for the good agreement between the two methods. The study revealed that UG students can be trained easily using easily affordable laboratory equipment and easily available reagents in low quantities. The green approach allows for use of smallest size and number of sample; use of miniaturized, energy efficient apparatus; safer operations; reduction in the volume of waste; and time savings.

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