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# Copper(II) Sulfate as a New Indicator Substitute to Phenolphthalein in Neutralization Titrimetry

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Copper(II) sulfate pentahydrate has been standardized as an advantageous indicator substitute to phenolphthalein in neutralization titrimetry. Copper sulfate 1000 $\mu g\ mL^{-1}$ titrand (*ca.* $2 \times 10^{-3}$ M near equivalence point) and phenlophthalein 10 $\mu g\ mL^{-1}$ titrand were compared as indicators for standardization of alkali hydroxides and mineral acids over the normality range 0.03 N to 1 N. The end-point with copper sulfate was sharp, and marked by appearance of a bluish-white turbidity, due to formation of cupric hydroxide near equivalence point, that did not disappear on shaking and standing. The mean normality values obtained with compared indicators did not differ significantly ($P > 0.1$). Copper sulfate offers certain advantages over phenolphthalein: it is water-soluble, the end-point is highly stable, and it may be used to measure titratable acidity of coloured solutions.

## INTRODUCTION

Neutralization titrimetry constitutes a powerful tool in analytical chemistry; it employs organic compounds as end-point indicators with colour change to mark equivalence point. Phenolphthalein is the most widely used end-point indicator in titrations involving strong alkali hydroxides. A need was mooted to search for a new indicator as a substitute to overcome limitations inherent in phenolphthalein use[1], notably its water insolubility and unstability of end-point.

The rationale for the present investigation has been based on the following considerations: (i) titrations involving alkali hydroxides exhibit a sharp pH shift at equivalence point from pH 4 to 10 in case of strong base-strong acid titrations, and from pH 6.5 to 10 in case of strong base-weak acid titrations; the fact that enables the use of phenolphthalein with working range 8.2 to 9.8 as a choice indicator in such titrations[2, 3]; (ii) copper(II) sulfate in presence of alkali hydroxides forms sparingly soluble cupric hydroxide at pH 6 and above[4], thus enabling the use of copper sulfate to detect equivalence point with turbidity to mark end-point; (iii) solubility product constant of cupric hydroxide is very low[5], $1.6 \times 10^{-19}$, thus small amounts of hydroxide ions will be required to induce

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*Correspondence address: Dr. S.A. Mir, Professor and Head, Department of Pharmacology and Toxicology, F.V.Sc. and A.H., Shuhama, Post Box No. 1310, GPO, Srinagar, Kashmir, India visible turbidity at equivalence point (iv) turbidity end-point is quite stable *per se*, and could be reversed by addition of known amount of acid, and back-titrated if required and (v) water solubility of copper(II) sulfate would be an additional advantage as it would obviate the use and interference of ethanol required as a solvent for phenolphthalein indicator[1, 6].

Accordingly, investigations were designed to conduct standardizations of alkali hydroxides, *viz.*, NaOH and KOH against primary standard succinic acid, and of mineral acids, *viz.*, HCl, $H_2SO_4$ and $HNO_3$ against secondary standard NaOH over the normality range 0.03 to 1 N in presence of copper(II) sulfate and phenolphthalein as end-point indicators.

## EXPERIMENTAL

The chemicals used were of high purity. The experiments were carried out at an ambient temperature of 15 ± 1°C. Double distilled water, freshly boiled and cooled, was used for dilutions, washings and preparation of reagents. Volumetric glassware used were pre-calibrated. Weighing error was 0.008 per cent for preparing stock 1 N solutions. Stock solutions of 1 N strength were prepared accurately for succinic acid, and approximately for alkali hydroxides and mineral acids. Other strengths, 0.3 to 0.03 N, were prepared from the stock solutions by dilution. Acids were always used as titrands, and alkali hydroxides as titrants. Different sized aliquots, 10 to 20 mL, of titrands were taken to avoid prejudiced end-points[7]. Aliquot sizes were matched for both indicators. Phenolphthalein 0.1% (w/v) in ethanol was added as 0.01 mL $mL^{-1}$ titrand, and copper(II) sulfate 10% (w/v) in water was added as 0.01 mL $mL^{-1}$ titrand to provide 500 μg $mL^{-1}$ $CuSO_4{\cdot}5H_2O$ (*ca.* $2 \times 10^{-3}$ M) at equivalence point.

Alkali hydroxides of respective strengths were first standardized against corresponding strengths of primary standard succinic acid. Standardized sodium hydroxide solutions were then used to standardize mineral acids of corresponding approximate normalities. Six observations were taken at each of the standardizations in presence of either indicator; three titrations conducted by each of the investigators to avoid any bias. For phenolphthalein, appearance of a faint pink coloration within 30 seconds that did not disappear on shaking was taken as an end-point. For copper sulfate, appearance of a faint bluish-white turbidity that did not disappear on shaking, and that intensified on standing was taken as an end-point. If inadvertently excess alkali got added to the titration mixture containing copper sulfate as indicator, a known amount of acid was added to dissolve cupric hydroxide and titration continued till a drop of titrant imparted visible turbidity to otherwise clear solution.

Acidity of copper(II) sulfate solution *per se* was determined by taking 10 and 20 mL portions of copper sulfate solution, 500 and 1000 μg $mL^{-1}$ water, and titrated against standard NaOH solution. In one experiment copper(II) acetate monohydrate 800 μg $mL^{-1}$ titrand (*ca.* $2 \times 10^{-3}$ M near equivalence point) was used as an indicator, and compared with copper(II) sulfate pentahydrate for standardization of 0.3 N $H_2SO_4$ against 0.3 N standard NaOH solution to test whether nature of copper salt had any effect or not.

Students' t-test was used to test any significant difference between mean values obtained with the two indicators. The relative mean errors of values obtained with copper(II) sulfate were calculated as per cent deviations from mean values obtained with phenolphthalein to estimate accuracy[4]. Precisions of the data were tested by using F-test.

## RESULTS AND DISCUSSION

Copper(II) sulfate *per se* showed negligible acidity, and negligible amount of sodium hydroxide was required to induce visible turbidity at equivalence point. Copper(II) sulfate pentahydrate 500 and 1000 $\mu g\ mL^{-1}$ water consumed sodium hydroxide, respectively, 0.000235 ± 0.000009 N (n = 12) and 0.000575 ± 0.000025 N (n = 18) to produce visible turbidity. There was no significant difference between 10 mL and 20 mL aliquot sizes ($P > 0.1$). Besides standardization of $H_2SO_4$, approximate strength 0.3 N against 0.3 N NaOH with either copper sulfate or copper acetate (*ca.* $2 \times 10^{-3}$ M copper ions at equivalence point, each) yielded comparable values, respectively, 0.3092 ± 0.0005 N and 0.3093 ± 0.0006 N with no significant difference between the mean values ($P > 0.1$). This indicated that the nature of water soluble copper salt had no effect on standardization at least for strong acid-strong base titrations, and either could be employed as an indicator.

The results (Tables 1 and 2) indicate that whether the titration was between alkali hydroxides and succinic acid, or between alkali hydroxide and mineral acids, the mean normality values obtained with either indicator were comparable over tested normality range 0.03 to 1 N, and no significant difference exists between compared sets of data ($P > 0.1$). Oxalic acid is not a suitable primary standard while using copper sulfate as an indicator as the two chemicals react to form insoluble copper(II) oxalate that interferes with the titrations.

TABLE-1

STANDARDIZATION OF ALKALI HYDROXIDES USING COPPER(II) SULFATE OR PHENOLPHTHALEIN AS INDICATOR

| Primary standard, N | Indicator | Alkali hydroxides, N | |
|---|---|---|---|
| | | NaOH | KOH |
| Succinic acid | | | |
| 0.03 | Copper sulfate (C) | 0.0268 ± 0.0002 | 0.0338 ± 0.0002 |
| | Phenolphthalein (P) | 0.0267 ± 0.0001 | 0.0335 ± 0.0001 |
| 0.10 | C | 0.1033 ± 0.0005 | 0.0931 ± 0.0003 |
| | P | 0.1032 ± 0.0003 | 0.0931 ± 0.0003 |
| 0.30 | C | 0.3047 ± 0.0003 | 0.2965 ± 0.0004 |
| | P | 0.3048 ± 0.0003 | 0.2974 ± 0.0003 |
| 1.00 | C | 1.0207 ± 0.0045 | 1.0681 ± 0.0018 |
| | P | 1.0252 ± 0.0043 | 1.0670 ± 0.0018 |

The values are mean ± S.E. of six observations, $P > 0.1$

TABLE-2
STANDARDIZATION OF MINERAL ACIDS USING COPPER(II) SULFATE OR PHENOLPHTHALEIN AS INDICATOR

| Secondary standard, N | Indicator | Mineral acids, N | | |
|---|---|---|---|---|
| | | HCl | $H_2SO_4$ | $HNO_3$ |
| Sodium Hydroxide | | | | |
| 0.03 | C | 0.0325 ± 0.0001 | 0.0303 ± 0.0001 | 0.0363 ± 0.0002 |
| | P | 0.0323 ± 0.0001 | 0.0301 ± 0.0001 | 0.0360 ± 0.0001 |
| 0.10 | C | 0.0929 ± 0.0002 | 0.1173 ± 0.0003 | 0.0984 ± 0.0002 |
| | P | 0.0928 ± 0.0002 | 0.1177 ± 0.0004 | 0.0985 ± 0.0003 |
| 0.30 | C | 0.2664 ± 0.0009 | 0.3092 ± 0.0005 | 0.3054 ± 0.0008 |
| | P | 0.2668 ± 0.0010 | 0.3088 ± 0.0006 | 0.3051 ± 0.0007 |
| 1.00 | C | 0.9270 ± 0.0014 | 0.9542 ± 0.0020 | 0.9867 ± 0.0020 |
| | P | 0.9270 ± 0.0019 | 0.9542 ± 0.0020 | 0.9867 ± 0.0031 |

The values are mean ± S.E. of six observations, $P > 0.1$.

Near the equivalence point only a drop of the titrant was required to induce visible turbidity in an otherwise clear solution. Thus, end-point with copper sulfate is sharp and easily obtainable. Besides, whereas phenolphthalein based end-point usually faded on prolonged standing, that due to copper salt intensified owing to growth of cupric hydroxide precipitate. This is an obvious advantage while using copper(II) sulfate as an indicator compared to phenolphthalein.

The mean values obtained with the copper salt as an indicator are highly accurate[4] as relative mean error was found to be less than 1% with respect to those obtained with phenolphthalein at all titration levels. An overall relative mean error including all titrations has been 0.34 ± 0.08 ($n = 20$), and relative mean errors at 1, 0.3, 0.1 and 0.03 N titrations have been, respectively, 0.37 ± 0.17, 0.14 ± 0.04, 0.15 ± 0.05 and 0.81 ± 0.11 ($n = 5$, each). The difference in accuracy between succinic acid-alkali hydroxides (0.29 ± 0.10 relative mean error, $n = 8$) and alkali hydroxide-mineral acids (0.37 ± 0.11, $n = 12$) is not significant ($P > 0.1$). The relative standard deviations (RSD) with copper sulfate and phenolphthalein have been found, respectively, to be 0.76 ± 0.09 and 0.66 ± 0.05 ($n = 20$, each). There is no significant difference in precision between two sets of data ($P > 0.1$). The RSD (mean ± S.E.) at 1, 0.3, 0.1 and 0.03 N level titrations, phenolphthalein *vs.* copper sulfate, have been found to be, respectively, 0.64 ± 0.11 *vs.* 0.58 ± 0.13, 0.49 ± 0.12 *vs.* 0.49 ± 0.11, 0.72 ± 0.05 *vs.* 0.73 ± 0.12, and 0.80 ± 0.10 *vs.* 1.24 ± 0.20 ($n = 5$, each). There is no significant difference in precision between comparable sets of data whether alkali hydroxides are titrated against succinic acid ($P > 0.05$, $n = 8$) or mineral acids are titrated against standard sodium hydroxide ($P > 0.05$, $n = 12$). It can be concluded that the mean values obtained with copper sulfate as indicator are as precise and accurate as those obtained with phenolphthalein. However, apparent precision with either indicator is relatively poorer at 0.03 N titration levels.

The present report is the first of its kind to use an inorganic salt as an indicator in neutralization titrimetry with turbidity as an end-point. Till date indicators used for the purpose have been solely organic chemicals with colour change to mark end-point. The favourable points that enable copper(II) sulfate to function as an indicator are: (i) formation of cupric hydroxide precipitate near equivalence point[4], and (ii) very low solubility product constant of cupric hydroxide at neutral pH[5]. The practical advantages of the present work are obvious: water solubility of the copper salt, stability of the end-point, and suitability in measuring titratable acidity of colored clear solutions. The rationale and technique has been employed for developing a new acidimetric assay for copper(II) sulfate[8], and for alkali nitrite (unpublished).

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