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# Semi-Microdetermination of Some Phenols with Ammonium Metavanadate(V) Reagent

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The semi-micro determination of some phenols with ammonium metavanadate(V) reagent has been done.

## INTRODUCTION

The phenolic function is characterised by the hydroxyl group attached to the benzene skeleton. Moss and coworkers[1] have estimated phenols like resorcinol, salicylic acid and hydroxy benzoates by potentiometric titrations using antimony electrode. Certain methods available for the determination of phenolic compounds are based on halogenation[2]. Non-aqueous alkalimetry[3], oxidimetry[4], nitrosation[5], esterification[6], gravimetry[7] and gasometry[8]. Shenk and Fritz[9] devised macro procedure for the determination of phenols by acetylation using perchloric acid as a catalyst. Mlodecka[10] evolved a bromometric procedure for the determination of phenols and cresols. Calorimetric methods have also been recommended for the microdetermination of phenolic compounds. The most sensitive method[11] for the calorimetric estimation of phenolic function is based on its reaction with 2,6-dichloro or 2,6-dibromo quinone chlorimine in alkaline solution. Celap and Janjic[12] used ring calorimetric method for the determination of micro amount of phelols. Popa and Stan[13] used spectrophotometric method for the determination of phenols. Mishra[14] have proposed a spectrophotometric method for the determination of phenol, catechal, resorcinal and pyrogallal.

A survey of literature reveals that vanadium(V) reagent has not been used for the determination of phenols till now. Vanadium(V) reagent used as a strong oxidising reagent. This inspired us to undertake present study. In this work we have developed a quick and convenient method for the microdetermination of some phenols like resorcinol, catechol, 2-nitrophenol 4-nitrophenol, 2-4-dinitrophenol, *o*-amino phenol, *m*-amino phenol, *p*-amino phenol, *o*-cresol and *m*-cresol.

## EXPERIMENTAL

### Reagents and Solutions

Reagent ammonium metavanadate (BDH) 3.5 g accurately weighed

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was dissolved in 10 ml of concentrated sulphuric acid (AnalaR sp. gr. 1.84) in the 100 ml volumetric flask and made up to the mark with distilled water. Stock solution of different compounds (1 mg/1 ml) were prepared by dissolving 50 mg of the pure compound in 50 ml volumetric flask in distilled water.

**General Procedure**

Aliquots containing 1.5 mg of the samples were taken in a 100 ml Erlenmeyer flask followed by the addition of 2 ml of 0.3 N vanadium(V) reagent and 5 ml of 8 N-sulphuric acid. The reaction contents were shaken gently and kept on a boiling water bath for a prescribed reaction time as fifteen minutes for resorcinol, catechol, 20 minutes for *o*-nitro phenol, *p*-nitrophenol, 2,4-dinitro phenol and 25 minutes for *o*-amino phenol, *p*-cresol. After the reaction was over the reaction mixture was cooled to room temperature. The unconsumed vanadium(V) reagent was titrated against 0.025 N ferrous ammonium sulphate, using N-phenol anthranilic acid as an indicator.

A blank experiment was also run under identical conditions using all the reagents except the sample. Recovery of the sample was calculated by following expression.

$$\text{mg of the sample} = \frac{M \times N(B - S)}{n}$$

where, M = Molecular weight of the sample.

N = Molarity of ferrous ammonium sulphate.

B = Volume of ferrous ammonium sulphate consumed to titrate in the blank experiment.

S = Volume of ferrous ammonium sulphate consumed to titrate in the same experiment.

n = Number of moles of vanadium(V) reagent consumed per mole of the sample.

A consolidated table is given which describes the results obtained with all phenols. For evaluating results on an accurate scale and testing the utility of the method, a large number of experiments were carried out and different variables were calculated. Standard deviation and coefficient of variation was also calculated. For calculating standard deviation in a particular estimation the experiment has to be repeated for several times. For each sample size about 10 to 12 estimations are done and the values having less variation in percentage recovery are noted. At least 9 such readings are selected and the results are recorded for each sample size. Ranging from 1 to 10 mg the same practice is adopted.

Standard deviation is calculated by following expression :

$$\text{S.D.} = \frac{(X_1 - X)^2 + (X_2 - X)^2 + (X_3 - X)^2 + \ldots + (X_n - X)^2}{(n - 1)}$$

where, $X$ = Mean value or average value of the amount obtained by calculation.

$X_1, X_2, X_3$ = Amount obtained by calculation.

After getting standard deviation values, the coefficient of variation is also calculated by the following expression:

$$\text{Coefficient of variation} = \frac{\text{S.D.} \times .100}{X}$$

where, $X$ = Mean value or average value of the amount obtained by calculation.

## RESULTS AND DISCUSSION

The effect of variables such as reaction time, reagent concentration, volume of sulphuric acid and temperature were studied. It was noticed that resorcinol and catechol takes 15 minutes, *o*-nitro phenol, *p*-nitro phenol and 2,4-dinitro phenol need 20 minutes, *o*-amino phenol, *p*-amino phenol, *m*-amino phenol, *o*-cresol and *p*-cresol need 25 minutes for complete reaction. Much more reaction time needed for *m*-amino phenol, *o*-cresol and *m*-cresol is due to presence of benzene ring. Further increase in the reaction time does not give any improvement in the stoichiometry as well as in the recovery of the sample. To enhance the reactivity of the reagent and to get quick reaction the ionic reaction medium was tested. It was found that the presence of 5 ml of 8N sulphuric acid is essential to provide ionic medium to vanadium(V) 0.3 N reagent. A low concentration of sulphuric acid although helps in reaction but gives inaccurate results. Incomplete reaction may be due to incomplete ionisation of vanadium(V) reagent. A higher concentration of sulphuric acid is a wastage and unnecssary. Moreover a higher concentration of sulphuric acid tends to give inconsistent results. After studying the variation in the concentration of vanadium(V) reagent it was found that 0.3 N concentration of vanadium(V) reagent is sufficient for quantitative results. A lower concentration tends to give lower result because of incomplete results while higher concentration is a wastage of the reagent. A large difference in the titre values of the blank and the actual experiment because higher concentration of vanadium(V) may also add to inaccuracy.

Stoichiometric determination shows that resorcinol, catechol consume two equivalent of vanadium(V) reagent at reaction time of 15 minutes and *o*-nitro phenol, *p*-nitro phenol and 2,4-dinitrophenol takes 4 equivalent of V(V) at 20 minutes reaction time and *o*-amino phenol, *p*-amino phenol, *m*-amino phenol consume 10 equivalent of van adium(V) reagent

TABLE 1

MICRODETERMINATION OF SOME PHENOLS WITH VANADIUM(V) (0.3N) REAGENT

| Sample's name | Amount taken (mg) | Amount present (mg) | Reaction time (min) | Amount obtained by calculation (mg) | Molecularity | Error % | Standard deviation | Coefficient of variation |
|---|---|---|---|---|---|---|---|---|
| 1. Resorcinol | 5 | 5.010 | 15 | 4.9825 | 2 | −0.55 | 0.0316 | 0.6296 |
| | | | | 5.0365 | | +0.53 | | |
| | | | | 5.0380 | | +0.56 | | |
| 2. Catechol | 5 | 5.010 | 15 | 4.9705 | 2 | −0.79 | 0.0448 | 0.8920 |
| | | | | 5.0475 | | +0.75 | | |
| | | | | 5.0490 | | +0.78 | | |
| 3. *o*-Nitro phenol | 5 | 5.010 | 20 | 4.9640 | 4 | −0.92 | 0.0468 | 0.9310 |
| | | | | 5.0580 | | +0.96 | | |
| | | | | 5.0575 | | +0.95 | | |
| 4. *p*-Nitro phenol | 5 | 5.010 | 20 | 4.9675 | 4 | −0.86 | 0.0432 | 0.8598 |
| | | | | 5.0515 | | +0.83 | | |
| | | | | 5.0545 | | +0.89 | | |
| 5. 2,4-Dinitrophenol | 5 | 5.015 | 20 | 5.0560 | 4 | +0.92 | 0.0471 | 0.9373 |
| | | | | 4.9620 | | −0.96 | | |
| | | | | 5.0565 | | −0.93 | | |
| 6. *o*-Amino phenol | 5 | 5.015 | 25 | 5.0596 | 10 | +0.89 | 0.0426 | 0.8470 |
| | | | | 4.9724 | | −0.85 | | |
| | | | | 5.0566 | | +0.83 | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 7. | *p*-Amino phenol | 5 | 5.015 | 25 | 5.0541 | 10 | +0.78 | 0.0380 | 0.7557 |
| | | | | | 4.9774 | | −0.75 | | |
| | | | | | 5.0531 | | +0.76 | | |
| 8. | *m*-Amino phenol | 5 | 5.015 | 25 | 5.0626 | 10 | +0.95 | 0.0561 | 01.1151 |
| | | | | | 5.0636 | | +0.97 | | |
| | | | | | 4.9659 | | −0.98 | | |
| 9. | *o*-Cresol | 5 | 5.015 | 25 | 4.9709 | 10 | −0.88 | 0.0435 | 0.8650 |
| | | | | | 5.0576 | | +0.85 | | |
| | | | | | 5.0581 | | +0.86 | | |
| 10. | *p*-Cresol | 5 | 5.015 | 25 | 5.0581 | 10 | +0.86 | 0.0481 | 0.9563 |
| | | | | | 5.0566 | | +0.83 | | |
| | | | | | 4.9739 | | −0.82 | | |

In each case three determinations were done.

at reaction time of 25 minutes, and *o*-cresol and *p*-cresol also consume 10 equivalent of vanadium(V) reagent at reaction time of 25 minutes.

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