Utilization of Used-Up Consumer Product Dry Cell for Developing New Experiment

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***Abstract* - As an alternative to the regular experiments dealing with analysis of an ore, an experiment is developed based on titrimetric analysis of some used-up consumer product. The determination of manganese from the electrolyte powder in a run-down dry cell by Volhard's method is an alternative for analysis of pyrolusite ore. The student may later think about the relationship between the properties and composition of the material also. The experiment may be successfully incorporated in the practical course for undergraduate students of Analytical and Inorganic Chemistry. The results of present work indicate the importance of composition with reference to amounts of manganese (IV) oxide, graphite, ammonium chloride (and zinc chloride) where MnO2, seems to be the major constituent of the dry cell.**

***keywords* - Chemistry Education, Pedagogy, Low Cost Experiment, Pyrolusite, Determination of manganese dioxide, dry cell**

I. INTRODUCTION

Battery is made up of a number of electric dry cells and is useful to supply electricity to small portable electrical appliances as torches, flashguns and transistor radios. The dry cell is a "primary cell" (a device operating irreversibly for converting chemical energy into electrical one). It is a modified 'Leclanche' cell as it has electrolyte in the form of paste or powder that also incorporates the depolarizer (a substance which prevents reaction products from interfering with cell reaction). It is called as "standard round carbon-zinc cell" as it consists of a carbon rod surrounded by manganese (IV) oxide and carbon powder and a zinc metal case with a 'gel' or 'moist paste' of ammonium chloride [**1**]. (The paste also may contain zinc chloride [**2**]. The nominal voltage of the cell is 1.5 V and the reactions within it although seem simple, are certainly more complex than those indicated [**3,4**].

The used-up or run-down dry cells may serve as a source of MnO_2, to do an experiment - "determination of manganese by Volhard's method". The electrolyte from cell may be considered as an alternative source for MnO_2, than the pyrolusite ore. The experiment for students is set here using seven samples of dry cells (pencil cells and torch/multipurpose cells of common size). The present paper is such that the student of chemistry may get its benefit in learning of some experiments developed involving analysis of common used-up consumer products. A theoretical and general back- ground, detailed procedure, calculations as well as representative result of actual analyses are done.

II. BACKGROUND FOR MANGANESE FROM ELECTROLYTE OF RUN-DOWN DRY CELL

Isolation of sample

The used-up dry cell is opened systematically using hack saw because the outer coats of cell are too much tightly packed or attached to each other. This is because of the chances of spillage of material if the cell ruptures somewhere. The electrolyte materiel contains moisture due to formation of water in the chemical reactions in working of cell. So it is dried in a desiccator, for overnight, prior to analysis.

Disintegration of sample

The electrolyte material containing MnO_2 and graphite is treated with aquaregia [**5-8(a)]** to convert MnO_2 and Mn_2O_3 to $MnCl_2$. After the treatment with concentrated sulphuric acid, $MnCl_2$ is converted to $MnSO_4$, which goes in solution, whereas the graphite remains unaffected. This solution is filtered off to eliminate from the filtrate the insoluble graphite material completely. Its presence is not favorable due to adsorbing nature and reducing character. The filtrate and washings are diluted to known volume and an aliquot of this solution is used for determination of manganese.

Determination of manganese as MnO_2

Volhard's method is employed [**5 (a),6]** for this, which is based on the principle that when warm solution of Mn (II) ion is treated with standard solution of potassium permanganate, the Mn (II) ions are oxidised and MnO_4^-, ions are reduced to give hydrated precipitate of MnO_2.

$3Mn^{2+} + 2MnO_4^- + 2\ H_2O \rightarrow 5\ MnO_2 + 4H^+$

This chemical reaction [**7]** indicates that

1 mole $KMnO_4$ = 3/2 atoms of Mn = 3/2 moles of MnO_2

.'. 1 equivalent $KMnO_4$ = 3/10 atoms of Mn = 3/10 moles of MnO_2

1000 mL 1 N $KMnO_4$ = (3/10) * 54.94 g Mn = (3/10) * 86.94 g MnO_2

1 mL 1 N $KMnO_4$ = 0.01648 g Mn = 0.02608 g MnO_2

1 mL 1 N $KMnO_4$ = 26.08 mg MnO_2
This relation is useful for calculations.
For this titration, zinc oxide paste is used in presence of dilute nitric acid. This is due to following reasons:
1. Hydrated MnO_2, (precipitated) has acidic properties and adsorbs $Mn(OH)_2$ preventing complete oxidation of Mn (II). The sufficient amount of ZnO minimizes the adsorption.
2. It precipitates iron and other impurities in manganese salt and the precipitate settles down very quickly.
3. It neutralizes H_2SO_4, added during the preparation of Mn (II) solution. The reaction requires neutral pH and ZnO helps for that.
4. The precipitate of MnO_2, forms colloidal solution or gel. The adsorption of MnO_2, on ZnO helps to get clear end point.
5. It avoids the formation of $KMnO_4$ as well as manganous manganate [Mn (MnO_4)] during the titration.
For the standardization of $KMnO_4$ using sodium oxalate (which forms oxalic acid prior to titration) the relation as

III. EXPERIMENTAL

For this experiment all the reagents and chemicals used are of AR or equivalent grade. The solutions have been prepared in distilled water (or in distilled and purified organic solvents wherever required).

Reagents

Disintegration of sample:
Concentrated acids: Hydrochloric acid, Sulphuric acid, Nitric acid
Determination of manganese:
Sulphuric acid (3 M): 84 mL of conc. H_2SO_4 is diluted to 500 mL.
Nitric acid (2 M): 12.5 mL of Conc. HNO_3 is diluted to 100 mL
Potassium permanganate solution (~ 0.025 N): About 3.55 g of $KMnO_4$ is dissolved in ~ 500 mL of water. The solution is warmed and then filtered. The filtrate is then diluted to 5 litre.
Standard sodium oxalate solution (0.025 N): 0.4188 g of anhydrous $Na_2C_2O_4$ is dissolved and then diluted to 250 mL exactly.
Zinc oxide paste (emulsion)

Procedure:

Standardization of $KMnO_4$ solution (~0.025 N): An aliquot of 10 mL of standard sodium oxalate solution (0.025 N) is taken in the titration flask. After adding 10 mL of sulphuric acid (3 M) it is warmed and titrated against $KMnO_4$ solution until the permanent pink colour is obtained. From the titration reading exact normality of $KMnO_4$ solution is calculated.
In the present experiment, for 10 mL aliquot of $Na_2C_2O_4$ (0.025 N) mean titration reading = 9.9 mL of $KMnO_4$ and exact normality of $KMnO_4$ = 0.02525 N

Isolation of sample:

The used up dry cell is first weighed as it is. After cutting with a hacksaw the outer coverings of the cell are removed one after another in a careful manner. The homogeneous material containing MnO_2 and graphite is taken out in a clean watch glass and weighed. The weight of the cell and the electrolyte in it are not required for analysis as such, but from them one may get an approximate idea about the amount of MnO_2, present per dry cell.

Disintegration of sample:

An amount of ~ 0.35 g of the dried material is weighed accurately in a 100 mL conical flask and covered with a stem-cut funnel. To it is added about 20 mL of concentrated hydrochloric acid followed by 5 mL of concentrated nitric acid. The mixture is heated in a fuming chamber on the low flame of the burner for a minimum of 30 minutes. On cooling the solution, 5 mL of concentrated sulphuric acid is added slowly to it. The flask is heated again till the white dense fumes of sulphur trioxide are evolved. The flask is cooled and the contents are diluted to ~ 80 mL with water. The solution is filtered through ordinary filter paper and residue is given washings till free from acid. The filtrate and washings are diluted together to 250 mL in a volumetric flask with water. The residue is rejected.

Determination of manganese from diluted solution of electrolyte

An aliquot of 10 mL of the diluted solution is pipette out in a 10 mL conical flask. To it is added slightly excess (~5 mL) of ZnO paste. The solution is heated to ~ 60 °c. To the hot solution are added 2-3 drops of HNO_3 (2 M) and it is titrated against previously standardized $KMnO_4$ solution (0.02525 N) with constant swirling until faint pink colour persists to the supernatent liquid. (To see the colour of supernatent liquid, it is necessary to allow the precipitate to settle). The details of the first trial (out of two trials) of analysis of electrolyte from sample D1 are given as a representative case.

IV. RESULT

Dry cell sample, D1

Weight of the dry cell = 17.3464 g
Weight of MnO_2 + graphite = 6.3439 g
Weight of sample, for analysis = 0.3995 g
For Volhard's method the mean burette reading = 12.5 mL $KMnO_4$ (0.02525 N)
1 mL 1N $KMnO_4$ = 26.08 mg of MnO_2
12.5 mL 0.02525 N $KMnO_4$ = 8.237 mg MnO_2
The aliquot (10 mL) of diluted solution contains 8.237 mg MnO_2
250 mL diluted solution = 205.9 mg of MnO_2
i.e. 0.3995 g of sample = 205.9 mg of MnO_2 or 0.2059 g of MnO_2
Percentage of MnO_2 in the sample = 51.53

All the results of various samples are summarized in Table 1.

V. CONCLUSION

The percentage of MnO_2, in dry cells is in the range 40 - 60 % and it varies somewhat as per change in the type or the brand of the cell. (The cell with paper casing seems to have more percentage of MnO_2, than that with metal casing).

The determination of MnO_2, from used-up dry cell introduces purposeful exercise - analysis of a consumer product using titrimetry. This experiment not only familiarizes the students with redox titrations (permanganatometry), but increases their awareness also about chemistry in working as well as analysis of consumer products. The analysis of dry cells of different types and of different manufacturing companies adds to the variety in laboratory work. The final results indicate the importance of composition with reference to amounts of manganese (IV) oxide, graphite, ammonium chloride (and zinc chloride) where MnO_2, seems to be the major constituent. The determination of graphite and ammonium chloride may also be added as an extension of the analysis.

The dry cell was considered first as a source of zinc metal. It seems, however, difficult to get zinc from it. This is because the zinc sheet used in the dry cell is very thin and in the usage of the cell it gets almost consumed.

Table 1 Determination of MnO_2 in some run-down standard round carbon-zinc dry cells

Code number, type	**Average weight (g) and average electrolyte content of the cell (g)**	**Weight of sample taken for analysis (g)**	**Titer mL $KMnO_4$ (0.02525 N)**	**Calculated % MnO_2**	**Mean % MnO_2**
D1 R6 (UM 3 DG) (Pencil cell)	17.34640 6.3439	0.3995 0.3684	12.5 11.6	51.53 51.87	51.70
D2 R_{20} (U_M 1 DG) with metal casing	90.0500 54.2900	0.3682 0.3418	9.5 9.0	42.50 43.38	42.94
D3 R_{20} (U_M 1(P)) with paper casing	62.8000 36.8100	0.3168 0.3408	10.3 11.0	53.56 53.17	53.36
D4 R20 (UM 1(U)) with metal casing	86.7136 40.8173	0.3707 0.3538	10.7 10.2	47.55 47.49	47.52
D5 R_{20} (U_M 1 (P)) with paper casing	66.1400 40.3500	0.3138 0.3430	11.5 12.5	60.37 60.04	60.20
D6 R_6 (U_M-3 DG) (pencil cell)	17.5700 7.3400	0.3618 0.3832	8.7 9.4	39.61 40.41	40.01
D7 R_6 (U_M-3 U) (pencil cell)	15.8900 6.2700	0.3743 0.3980	9.5 10.0	41.81 41.39	41.60

VI. ACKNOWLEDGEMENT

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