Microscale Experiments in Chemistry – The Need of the New Millenium

3. Microscale Inorganic Qualitative Analysis and New Methods of Titrations for Introduction at All Levels in Chemistry Laboratories

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Introduction

In the earlier articles[1] we described some experiments which can be carried out in an organic laboratory. Inorganic qualitative analysis constitutes a major bulk in the syllabi of chemistry in academic programmes all over the country. Substantial amounts of inorganic chemicals, reagents and toxic gases like hydrogen sulfide (H_2S) are used during the experiments. The fumes of acids and smell of gases evolved or used during chemical reactions had always been a threat to the environment of all laboratories. The conventional method of qualitative analysis prescribes the use of about 0.2 g chemical for every test of the qualitative analysis. This seems to be out of date in the present context and needs a drastic revision.

We have adopted this scheme without any conceptual deviation from the principles of analysis and yet reduced the consumption of chemicals. The same analysis was carried out using apparatus similar to conventional ones but of a smaller size such as a few small droppers, Beral pipettes, spatula made from bicycle spokes and small test tubes. The method certainly saves time and energy of a student while performing the experiments. The best part of this method is the minimum use of obnoxious hydrogen sulfide gas. We tried this method with the help of volunteers from final year BSc students. During workshops, all teachers performed the qualitative analysis of inorganic mixtures themselves and appreciated it. A vast majority of them even suggested the introduction of these at the 10+2 level. A few colleges have already implemented it.

The Two Burette Titration

Among all the experiments performed by the students in our laboratories by the prevalent methods, titration is the most hazardous. In almost all laboratories throughout the country, the students at all levels are asked to pipette out solutions by mouth. Invariably, every day, many of them accidentally suck the chemicals into mouth. In some cases, students are not even told about which of the chemicals should be pipetted and which should not be! It is not unusual to see students sucking benzene or carbon tetrachloride or solutions of phenol, iodine and potassium permanganate by mouth and getting blisters inside the mouth. We felt that this unhealthy and hazardous method should be abandoned forthwith! One of us (SLK) recalled the 'two burette method' of titration from the laboratory manual of University of Wisconsin-La Crosse. We thought of adopting it with some better perspectives in mind.

The method excludes the use of any pipetting. Instead, both the titre and the titrant are taken in two different burettes A and B. For the titration about, 10 mL of the titre (It is not necessary to measure out exactly 10 mL. It could be any quantity provided the burette reading is recorded carefully and accurately.) is taken out from burette A. After adding a drop of the required indicator the solution is titrated against the titrant solution from burette B. The end-point is recorded when the indicator changes its colour. The reading of the burette B is recorded against that of burette A. To the same solution in the same flask then, further 1 or 2 mL of the titre is added from burette A. The colour of the solution changes back to the original since the titre

It is of interest to note that Mauritius, an island nation in Indian Ocean issued a postal stamp a few years ago, depicting students using mouth for pipetting. The wrong practice was pointed out vide a letter to the editor *Journal of Chemical Education*, 58, 293 A, 1981. It came to the fore further when the same journal published an article on 'Chemistry on Postal Stamps' in which information on various postal stamps issued by many countries on chemistry, chemists and unique contributions of the development of chemical sciences was published (*J.Chem.Ed.* 63, 285, 1986).

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[1] Part 1. Newer Ways of Teaching Laboratory Courses with New Apparatus, *Resonance*, Vol.5, No.10, p. 24, 2000.
Part 2. Experiments Which Bring Theory Closer to Laboratories, *Resonance*, Vol.5, No.6, p.6, 2000.

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from burette A is in excess. This solution is titrated once again with the titrant from the burette B. Readings of burettes A and B are recorded against each other. In this way, switching back and forth from burettes A and B, at least 7 to 8 readings could be recorded with just about 10 mL of each of the titre and titrant solutions. Rinsing of the flasks, repipetting by mouth or addition of fresh indicators for every titration is completely avoided, thus reducing the time required for performing the experiment and making the experiment safe. A few more advantages also accrue. In the currently practised method, if excess of titrant is added during titration, the entire titration has to be repeated. This is not required by the new method. If by mistake, one of the solutions is added in excess, one can take that as the initial reading and titrate the solution against the other. The normality of the unknown solution can be calculated mathematically ($N_1V_1=N_2V_2$) with each reading and then averaged or derived graphically by plotting a graph of readings of burette A vs those of burette B. From the slope and the strength of the known solution, normality of an unknown solution can be easily derived. The method thus saves the cost of chemicals by at least half. Results of a typical experiment and the method of calculations are shown later. We find this method not only safe but also accurate enough to the extent to which the students are expected to perform the conventional titrations. The time required to complete the titration experiment by this method is just about 10 to 15 minutes as against at least 45 to 60 minutes by the old method.

It had been the practice in the academic laboratories, that out of the four types of acid base titrations which should be performed for better understanding, only the one using strong acid against the strong base is usually done by the students at 0.1N concentration. Occasionally the titration of strong acid against weak base or weak acid against strong base is prescribed in the laboratory courses. The concepts of end point, neutralisation point and equivalence point along with the theory of indicators is taught in the classrooms. But experiments to verify these are never prescribed in the syllabi of laboratory courses. For all titrations, the students are 'instructed' to use a specific indicator. Without much explanation or reasoning, they are told to remember the choice of indicators in an empirical manner through coined phrases such as *SAM* (strong acid – methyl orange) and *WAP* (weak acid – phenolphthalein).

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With the new method of titrations, this scenario will change. With reduction in amounts and time, the students can now do many more titrations using same solutions and with as many indicators as they wish within the same laboratory period. They can now determine themselves which are the better indicators for any particular pair of titrant and titre, calculate the pH at which different indicators change the colour and observe that the end points in each would differ with different indicators. They would comprehend that end point, equivalence point and neutralisation point are different entities. During the experiments, we reduced the concentrations of the solutions to 0.05N and yet the results obtained were with desired accuracy and within the expected range of errors. It was also found that using similar technique and bromothymol blue as the indicator, the titration of a weak acid (acetic acid) and weak base (ammonium hydroxide) could be performed with accuracy and reproducibility. In many laboratories this experiment is avoided due to the non-availability and high cost of a suitable visual indicator. With the present method much less indicator will be needed, thereby reducing the cost significantly.

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The advantages are not restricted to only these experiments. Using the same 'two burette method', redox titration between potassium permanganate and oxalic acid with the former as the self-indicator could be performed with equal accuracy and reversibility if added in slight excess. In these titrations, reagents like diphenylamine, methylene blue, 1,10 phenanthroline, vanadium (II) etc. act as self indicators. While the transition range of pH determines the suitability of an acid-base indicator, the redox indicators are chosen according to their transition range of redox potential in volts. The difficulty sometimes is that many of these show mixture of colours, in the transition range, as it approaches the exact end point. The averaging of the end point comes much closer to the expected values by using the two-burette method. If actually practised, the students can learn about the suitability of indicators and check the reversible nature of the indicators by varying pH, temperature, and concentration of solutions by the new method.

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In many of our laboratories, iodometric titrations are considered separate from the redox titrations, mainly because, starch is used as indicator in place of the conventional ones. One of the requirements of these titrations is that starch is to be added not at the beginning but almost at the half-way stage of titration. It could be easily appreciated that starch can work as a reversible indicator during titrations like standardisation of sodium thiosulphate with potassium dichromate or estimation of copper in brass alloys.

Yet another type of titration is complexometric – using EDTA as the complexing agent. Eriochrome black-T is frequently used as the indicator in this experiment. Advantage is taken of the fact that in presence of EDTA, the initial complex formed by the metal with the indicator dissociates at the equivalence point. The indicator is set free and the colour of the complex changes to original color of the indicator, indicating an excess of the metal ion concentration. Most frequently, the stability of the complex is pH dependent. This factor along with the reversible nature of indicator can be studied more accurately using the 'two burette method'.

Precipitation titration used for the determination of concentration of halide ions employ adsorption indicators such as eosine, fluorosceine, rhodamine, etc. Usually silver nitrate is added in varied volumes in these titrations. The indicator gets adsorbed on the precipitate at the equivalence point and gives the characteristic colour. The 'two burette method' can check the dependence on pH of these indicators, along with their reversibility.

Titration by Drop Counting!

Taking clue from some of our articles published earlier in this series, we would now suggest that instead of using ‘two burette method’, two Beral pipettes can be used for titration, especially for the ones using expensive silver nitrate. Most of the methods published earlier suggest that the pipettes be weighed every time the solutions are taken in small amounts from them. This is quite tedious. Some others have even proposed that the existing capillaries of polymeric dropper pipettes be pulled further into still smaller capillaries. Obviously these were published when the polymeric Beral pipettes (henceforth mentioned as BP) were not easily accessible. They are available now, even in different colours, at a very affordable price of Re 1 each! Manufactured locally from low-density polypropylene, they are unbreakable, transparent and resistant to almost all chemicals including concentrated sulfuric acid. Using the old, redundant glass pipettes which require sucking of solutions by mouth, we ask the students to pipette out exactly 1 mL of water in a sample tube. Ironically, this will introduce them to the old method of using pipettes! The entire measured volume of liquid from the sample tube right up to the last traces can be taken into a BP as the capillary tip can reach out to the smallest possible drop in the sample tube. The bulb is then squeezed slowly so that the water comes out in drops, which are counted. The water thus taken out is collected in the same sample tube so that the quantity remains unchanged for counting the number of drops per mL and averaging. This gives the average volume of every drop of any BP. Statistically, we have found that the number of drops per mL remains same within a limit of 2-3% and so the average volume per drop is not affected. All the BPs, which are to be used for titration, can be calibrated in this manner. The acids and bases are then taken in separate calibrated BPs. One measures number of drops of acids from BP ‘A’ into a 10 mL Erlenmeyer flask or a small test tube, adds one drop of indicator and titrates this against the base added dropwise from BP ‘B’. After the end point is observed, a few more drops of acid from BP

Box 1. Typical Results from a Titration Experiment to Determine the Strength of an Unknown Acid.

Observation table for the 'two burette method'

Titration between HCl(strength unknown) and NaOH(exact strength 0.05N)

Indicator: phenolphthalein End point: pink → colourless → pink

Equation: $NaOH + HCl = NaCl + H_2O$

Reading	1	2	3	4	5	6	7	8	9
NaOH	10	11.2	12.5	13.2	14.6	16.0	17.1	18.5	19.8
HCl	10.4	11.7	13.0	13.8	15.2	16.8	17.6	19.2	20.5
N of HCl	0.048	0.047	0.048	0.047	0.048	0.0476	0.049	0.048	0.048

Calculations:

N_1*V_1 (NaOH) = N_2*V_2 (HCl) , $N_1*V_1/V_2 = N_2$ of HCl

Average normality calculated for HCl: 0.0478N

Observation table for titration using same solutions with two beral pipettes.

Beral Pipette	"A"	"B"
Number of drops per mL	34	39
Volume per drop	0.029mL	0.025ml
Containing solution	0.05N NaOH	HCl of unknown strength

Reading

No. of measurements	1	2	3	4	5	6	7	8	9
BP A (drops)	10	15	18	22	30	35	40	44	50
BP B (drops)	12	18	22	27	37	43	49	54	61
Normality of HCl	0.048	0.048	0.047	0.047	0.047	0.047	0.047	0.047	0.048

Calculations:

$$\frac{0.029*\text{number of drops of BP A}*0.05}{0.025*\text{number of drops of BP B}} = \text{Normality of HCl}$$

Average normality calculated for HCl: 0.0473N

Total amount of NaOH used in the two beral pipette method: 1.5 mL

'A' are added to the Erlenmeyer flask. The colour of the solution will obviously change. This solution can be retitrated in a similar way with drops from pipette 'B'. By multiplying the number of drops by the average volume determined earlier, the volumes of the titrant and titre can be obtained. The calculations of the normality of the unknown can be done in the usual manner. Both 'two burettes' and 'two BP' methods would require the same time for completion of the experiment. However, the amount of chemicals used in the BP titrations is much smaller – usually 1 to 2 mL. We can now prove statistically that there is hardly any difference in the results obtained. These titrations work out in the same range of errors allowed for students as in the conventional titrations.

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Many teachers feel that this will be a 'big leap' to go down from 40 mL to just about 2 mL of each solution in titration experiments. Under the circumstances, we feel that the Beral pipettes should be introduced at school level for doing many experiments including titrations and the 'two burettes' method at the colleges. Since the students achieve this with similar accuracy and reproducibility through the new methods using amounts as low as 5% of what is being currently consumed, the unconventional titration without burettes and pipettes should be acceptable to all.

Besides savings in time and money, the new methods open ways for a plethora of experiments, which would demonstrate many principles to the students and let them learn for themselves. They realise that the end points of a given titration as determined by various indicators are different, that different indicators change colours at different pH and that they may not get the correct equivalence point if they use the wrong indicator. Doing all this was not possible by conventional titrations particularly because of time constraints. Perfectionists might still worry about the 'accuracy' while using 'two burettes' against the accuracy of a pipette. However, it is important to realise that even a pipetted solution is not accurately measured since it is a func-

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tion of temperature and calibration. It is required that the advantages of the proposed methods be balanced against the shortcomings of the conventional methods. Logically the former will outweigh the latter. Further, if the shortcomings are within the practical limits, then it is better to go for inexpensive methods anyway.

Solution to

CROSSWORD PUZZLE No. 3
January 2001

1 L	A	2 U	D	3 A	N	U	4 M	▨	5 W	▨
E	▨	N	▨	V	▨	▨	6 E	C	H	O
7 S	P	I	K	E	▨	▨	T	▨	I	▨
B	▨	T	▨	8 S	E	9 C	A	10 N	T	▨
11 A	R	C	S	▨	▨	12 A	L	I	E	13 N
U	▨	E	▨	14 G	A	S	▨	C	▨	A
15 X	16 Y	L	17 E	M	▨	▨	18 S	O	L	S
▨	19 A	L	D	O	L	20 S	▨	T	▨	C
▨	H	▨	E	▨	▨	21 A	M	I	N	E
22 F	O	A	M	▨	▨	V	▨	N	▨	N
▨	O	▨	23 A	F	F	E	R	E	N	T