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Greener Qualitative Analysis for Anions in a Mixture

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ABSTRACT

The current study involves the participation of the disciplines of Chemistry and Psychology to investigate and highlight environmental pollution relating to the indoor air quality in a chemistry laboratory. The deteriorating air quality and fear of handling corrosive and toxic chemicals act as stressors having harmful physical and mental health consequences on students. Based on a survey conducted by us on about 300 undergraduate students to assess their awareness about hazards and toxicity associated with chemistry experiments, many hazardous and corrosive chemicals were identified which the students felt uncomfortable to use. We have tried to modify experiments involving such chemicals by using the principles of Green Chemistry. Qualitative analysis of inorganic mixtures is an essential part of the laboratory curriculum and the classical method of analysis involves use of large amounts of corrosive acids and various toxic chemicals. Heating with acids generate obnoxious fumes which deteriorate the indoor air quality; considerable amount of liquid waste is also produced which contaminates the water.By using selective ecofriendly spot tests we have made an effort to reduce the indoor air pollution, cut down the consumption of chemicals and minimize the waste produced. This greener alternative reduces the environmental pollution and the amount of waste generated thereby creating a safer ambience in the chemistry lab for our students. This scheme of analysis is simple, non-polluting, energy and time efficient.

Keywords: Anion analysis, Green Chemistry, ecofriendly, micro scale, spot tests

INTRODUCTION

Being of an era wherein the atmosphere is brimming with toxic gases, the aquatic system engulfed in irretraceable contamination and the flora and fauna in a presumable state of great peril; it should only be most appropriate on our part to morally extend our full support in ensuring a sustainable future that is in all ways beneficially habitable for each and every form of life. A student of chemistry is expected to perform a large number of reactions as per the practical curriculum. They are most evidently exposed to chemicals that may be detrimental to their health and daily performance, also it could be a matter of serious concern and might be the reason of chronic ill effects to health and psychology.Chemical reactions generate huge amounts of obnoxious fumes and cause deterioration of indoor air quality. An undergraduate chemistry laboratory runs for about 40 hours per week and the average amount of liquid waste generated daily is about 1000litres. The waste is a complex mixture of substances which is difficult to separate and reuse. Most of this is thrown down the sink and contaminates water. Commercial disposal of this waste is also an expensive proposition. Air and water pollution cause toxicological reactions, challenge homeostatic balance and produce physical trauma such as allergies, asthma as well as mental strain. Many students tend to shy away from the chemistry laboratory particularly when corrosive and toxic chemicals are handled.

The need of the hour is to ensure a safe and stress free chemistry laboratory for students, teachers and supporting staff. This was the focal point in the innovative project "A Green Chemistry Approach to Combat Stress in the Undergraduate Chemistry Laboratory" (GC201) involving the disciplines of Chemistry and Psychology. A survey was conducted on about 300 students and some faculty members of different colleges by using an open ended questionnaire prepared by the students of psychology. The aim was to assess the level of knowledge regarding toxic chemicals, indoor air pollution and safety measures adopted in a chemistry laboratory. Analysis of the responses revealed that second and third year students were more aware of pollution in a laboratory than the first year students. Major chemicals identified by them included cyanides, concentrated nitric and sulphuric acids, hydrogen sulphide, phosphorous pentachloride, pyridine, nitrobenzene, benzoyl chloride, bromine etc. which were seen as being linked to adverse health consequences. The students of chemistry then worked on replacing harmful chemicals used in certain experiments with safer alternatives using the 12 principles of Green Chemistry (1, 2).

Green chemistry began in 1991 at the EPA by Professor. Paul Anastas and Professor John Warner of the University of Massachusetts, Boston. It is defined as the design of chemical products and processes that reduces or eliminates the use and generation of hazardous substances, thereby reducing the detrimental effects on human health and environment.

Undergraduate education is an important level at the concepts of Green chemistry should be introduced.

Salient features of these concepts are:

- The best reaction is the one in which all the atoms of the reactants are incorporated in the product
- Starting reactants should be renewable and safe
- The product of one reaction be used as reactant of another; the reference is to waste minimization in particular
- Reaction should be observed at room temperature
- Alternative sources of energy should be used,
- A catalyst be used, preferably enzymes
- Green solvents be used e.g. water and no solvent is the best solvent

Green Chemistry basically aims at the safe and judicious usage of various chemicals and takes into consideration the concept of sustainable development. It has been instrumental in ensuring a safer working environment and reducing the stress level in students in handling and usage of chemicals. It is our aim to apply these concepts in our curriculum in a way that can ensure reducing toxicity to the minimal level, ensuring higher level of safety and fostering stress free processes.

The laboratory curriculum of developed countries has a greater focus on instrumentation whereas the developing countries, particularly South Asian countries, rely on classical techniques. Qualitative analysis of unknown inorganic mixtures is an important part of the chemistry curriculum at school, undergraduate and postgraduate levels in India and South Asian countries. The level of complexity varies; in the University of Delhi a student of B.Sc. Programme has to detect two anions and two cations in a mixture while a student of B.Sc. (Hons) Chemistry has to analyze a mixture for three anions and three cations. This type of training inculcates a systematic and logical approach to a problem, and is an excellent platform for correlation of theoretical principles with laboratory skills. The student at a later stage can extend this knowledge to the analysis of minerals, fertilizers, pharmaceuticals and other industrially important compounds. The classical method of analysis involves the use of corrosive acids and many toxic chemicals like hydrogen sulphide, lead and mercury compounds (3). The adverse effect of these on human health is well known (4). Heating and evaporation of acids generate dense fumes which deteriorate air quality and cause physiological problems.In a laboratory of 60 students, a few fume cupboards offer little help. Moreover if used, the fumes will anyhow be released to the atmosphere. The level of liquid waste generated is high resulting in water pollution. Most of the steps involve heating and this results in significant consumption of LPG. Concern about the environmental hazards caused by the chemistry laboratories of academic institutions has resulted in an attempt to design an ecofriendly scheme of analysis which will inculcate environmental awareness in the minds of young students and encourage them to use green practices in the laboratory as well as in life.

School students do the analysis at a macro scale where they use large amounts of chemicals; the consumption of heat energy, the waste generated and the extent of air pollution are high. In colleges the analysis is expected to be done at the semi micro level which saves on chemicals and time. During a survey conducted as a part of our project, we were startled to find that out of 22 colleges surveyed by us (in many cases students and teachers were reluctant to state many things in writing) only 10 colleges were doing analysis at the semi micro scale while others were doing it at the macro scale.It is important to reduce the consumption of chemicals, this will be economical, reduce waste generated and lower toxicity. Working with smaller amounts increases speed of analysis and also reduces pollution.

Experimental Development

The analysis of cations involves the use of the highly toxic hydrogen sulphide (H_2S). We have developed a green scheme of analysis for cations which totally does away with this chemical. This is published in the Journal of Chemical Education of the American Chemical Society (5). Students in various parts of India have used this scheme successfully.

The analysis of a mixture becomes complete if we are able to adopt a green method for detection of anions too.Spot tests have been developed for detection of anions which reduce the consumption of chemicals, minimize the use of toxic acids, increase efficiency and ensure certainty of analytical results. The reagents used are low cost and readily available.This saves on chemicals, time and heat energy as a single electric oven replaces 60 burners in a class size of 60.

A comparison of the amount of chemicals used in the conventional and green methods of analysis for a laboratory of 60 students is shown in Table I. We have only included some corrosive and toxic reagents used for identification. The list is long, only a few representative cases are shown. The toxicity of chromium (VI) and lead (II) compounds is well known.

Table- I Comparison of various chemicals used in the analysis

Chemicals used	Macro Analysis	Semi-micro Analysis	Modified by us using spot tests for anions
Sample for entire analysis	240 – 300g	60g	6g
Concentrated sulphuric acid	1500 ml	250ml	<25 ml
Potassium dichromate	30 g	7 g	<1 g
Lead acetate	30 g	7 g	< 1g

In one semester about 15 laboratory sessions are devoted to mixture analysis and 3 sections of students (total 180) perform this. This indicated a very high level of consumption of chemicals and an enormous amount of waste is generated. As chemists, we are primarily focusing on the environment but one cannot neglect the economic factor involved. The grant received for purchase of consumables remains static while the price shows an upward trend.
The advantages of the modified scheme are:

- Economical (cost saving is spectacular)
- Reduces air and water pollution
- Analysis is quick
- Saves on heat energy (Gargi College uses 80 cylinders of LPG in an academic year despite following semi micro analysis, one can imagine the figure if macro analysis was done)
- Reduce toxicity
- Creates safer working conditions
- Reduces stress

METHODOLOGY

The conventional tests in the macro scale are carried out in glass test tubes (20 ml capacity), in the semi-micro scale the size of the tube is reduced (4-5 ml) and about 1ml of the analyte is taken in each test. Spot tests are performed on grooved tiles, microtubes (ignition tubes) or on filter paper.
The white porcelain background enables ready perception of colourchanges. It is helpful to compare the colour change with a blank test carried out on an adjacent groove. If the reaction produces a white precipitate or turbidity, visualization on a white background becomes difficult. We have fabricated black grooved tiles from small pieces of granite (waste material from construction areas) and used them for detection of white precipitate. Alternatively if black tiles are not available these tests can be successfully carried out in micro tubes or on a transparent watch glass placed on a black paper.
For reactions performed on filter paper,a small strip (1x2 cm) of Whatman No. 1 filter paper is used. A spot of the detecting reagent (e.g., acidified potassium dichromate for sulphite,

lead acetate for sulphide) is introduced on the filter paper with the help of a capillary. In certain cases the filter paper is impregnated with the reagent and the dry impregnated paper is spotted with a drop of the analyte.

This method of detection is used for borate using turmeric paper. We prepared turmeric paper using raw turmeric which was peeled, cut into small pieces and the thick juice was extracted using an electric blender. A cotton swab was used to coat a sheet of Whatman No. 1 filter paper uniformly with this juice. This was dried in the sun and cut into strips of the desired size. The cost of 200 strips of self-prepared turmeric paper is only Rs. 20 in contrast to $22.20 in USA. (This test is not a common laboratory test in India, in USA it is generally used to detect borate and boric acid in food stuffs and swimming pools. It is also used for spectrophotometric determination of boron). We have found it to be a very sensitive test for borate.

For reactions that required heating, an electric oven maintained at 120^{o}C was used. Many anions are identified by the gases evolved by the treatment of the dry mixture with dilute and concentrated acids and the gases are detected with a specific reagent. In such cases a wire or a pin with a head was passed through the centre of 2 strips of filter paper, and the papers were not allowed to touch. A small amount of mixture (size of a rice grain) is placed on the lower paper and a drop of the testing reagent on the upper paper. The setup kept in a vertical position is heated in an oven and the colourchange noted. This procedure is successful for detection of sulphite, sulphide, nitrite and thiosulphate.Bromide, iodide and nitrate evolve coloured fumes when heated with concentrated sulphuric acid, in such cases the paper gets corroded with concentrated acid and it is better to perform the test with a rice grain of mixture in a micro tube.

The reagents used in conventional tests are used, they are readily available and found on the shelves of the laboratory table or side shelves. The conventional tests and spot tests are shown in table 2. In most cases the reagents used in conventional macro scale have been adopted for spot tests, thus the chemistry behind these tests is similar as in conventional classical analysis (3).A part of this work has been presented in an international conference and has been extremely well received by the delegates (6).

RESULTS

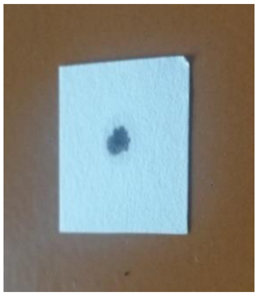
A large number of texts are available for qualitative inorganic analysis, but the standard text is written by A.I. Vogel which has stood the test of time and has been revised on numerous occasions (3). There is an exclusive book on spot tests (7), the reagents used are expensive, not readily available and most of them are organic compounds which are not ecofriendly. The novelty of this scheme is that besides being ecofriendly it involves adoption of reagents used in conventional analysis (macro or semi micro scale) to a micro scale. We are discussing a few representative cases, all tests are shown in Table IIwhich is self-explanatory. The brown ring test for nitrates is conventionally done in a test tube but the same is depicted beautifully in a grooved tile. Carbonates evolve carbon dioxide on treatment with dilute acids, the gas is passed through lime water using a specific apparatus (shown Table II).We have found that barium chloride works better than lime water. We have taken the mixture in a grooved porcelain tile and a drop of barium chloride in the tip of a dropper or a glass capillary held very near the groove. Addition of a drop of dilute acid evolves carbon dioxide which is noted by the solution in the dropper or capillary turning milky. The conventional test for borate involves use of the toxic and inflammable methanol and the corrosive sulphuric acid; moreover heating is needed. The turmeric paper test, on the other hand is done at room temperature and eliminates use of harmful chemicals. About 50 mixtures having various combinations of anions have been analyzed by our students and the results are reproducible.

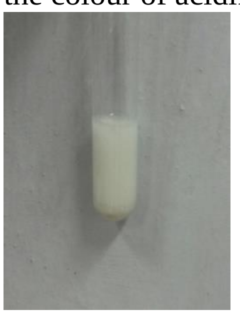
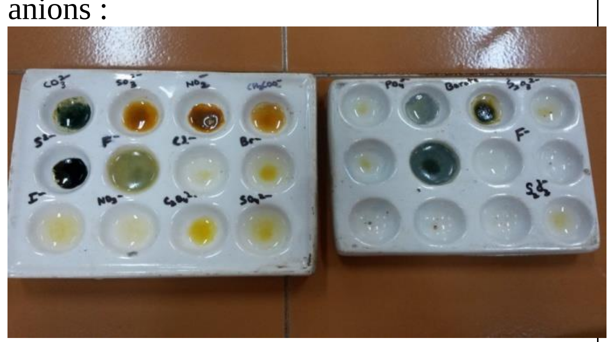
Safety is of utmost importance in a chemistry laboratory .and students at all levels are taught about this aspect. They are advised to tie their hair, wear a lab coat, closed shoes use safety glasses and amask. (Figure 1). Real World case studies are discussed in order to explain safety in a chemistry laboratory. We strongly recommend that students should be made aware of the hazards of an experiment and the toxicity levels (MSDS and CAS values) of the chemicals they will use. This knowledge will enable them to think critically and come up with novel green ideas. We wanted to use sensors to check the laboratory air quality before, during and after a session where a conventional and green method of analysis was used. This would have given a quantitative picture but due to paucity of funds the same could not be done.

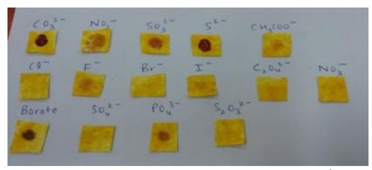
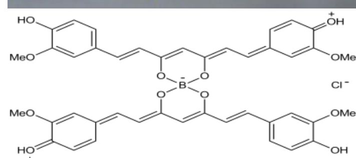
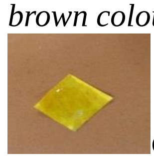
Figure - 1 Safety Measures practiced in Gargi College Chemistry Laboratory

Table – II Comparison of conventional and greener alternatives for various anions

Anion	Conventional method	Modified method
Carbonate	Mix + dil. H_2SO_4gives effervescence of CO_2(g) which turns lime water / $BaCl_2$ milky 	A rice grain of Mix + dil. H_2SO_4 taken on a groove tile. Tip of dropper containing $BaCl_2$ brought near it turns milky. 

Sulphite	Mix + dil H_2SO_4 in test tube, gas evolved on heating turns acidified $K_2Cr_2O_7$ paper green. 	Mix + dil H_2SO_4 on a paper turns acidified $K_2Cr_2O_7$ paper green (heated in an oven).  Magnified image is shown.
Nitrite	Water ext + sulphanilicacid + α-naphthylamine in test tube gives red colour 	Waterext+ sulphanilic acid+ α-naphthylamine gives red spot on filter paper . 
Sulphide	Mix + dil H_2SO_4 in test tube, gas evolved on heating blackens filter paper moistened with lead acetate solution.  Crude image, heating not shown	Mix + dil H_2SO_4 + lead acetategives ablack spot on filter paper. (heated in an oven) 

Chloride, bromide, Iodide	Na_2CO_3 ext. + dil. HNO_3 + $AgNO_3$: white precipitate, soluble in aq. NH_3 - Chloride Pale yellow precipitatepartially soluble in aq. NH_3 - Bromide Yellow precipitate insoluble in aq. NH_3 - Iodide 	Fabricated a grooved tile from black granite and performed test with 1 drop of test solution. White precipitateof AgCland pale yellow precipitateof AgBr was clearly visible.For iodide, white grooved tile was used. Solubility in aq. $NH_3$was checked asin the conventional method. 
Fluoride	Na_2CO_3 ext. + CH_3COOH + $CaCl_2(aq)$ gives white precipitate which discharges the colour of acidified $KMnO_4$  Mix. + borax + conc. H_2SO_4gives green flame on heating 	Acidified solution of fluoride discharges the red colour of iron thiocyanato complex prepared by treating ferric chloride with ammonium thiocyanate  $[Fe(H_2O)_6]^{3+}$ + 3 SCN^- → $[Fe(SCN)_3(H_2O)_3]$ $[Fe(SCN)_3(H_2O)_3]$ (red) + F^- gives $[FeF_6]^{3-}$ (colourless) The interference was checked with different anions :  None of the tested anions interfered.

Borate	Conventional method involves heating with conc. H_2SO_4 and alcohol and burning the vapours evolved. To the solid mixture in a test tube, conc. H_2SO_4 and methanol (or ethanol) was added. The test tube was heated on a flame and the vapours generated were directed to the flame. A green flame confirmed the presence of borate. Drawbacks : • Methanol and ethanol are highly inflammable organic solvents. • Conc. H_2SO_4 is corrosive. • Heat energy is used. 	<u>Test for borate using cheap, self prepared, acetone/ alcohol free turmeric paper</u> : This is not a widely used test in the laboratory and is generally performed for analysis of borate or boric acid in food stuffs and swimming pools. It is also used for spectrophotometric determination of boron. Commercial turmeric paper :200 strips -$22. Self prepared paper:200 strips -Rs. 20 Borates in 2N HCl and boric acid give a red-brown complex due to the formation of rosacyanine. Rosocyanine is formed as 2:1 complex from curcumin and boric acid in acidic solutions.   The rosacyanine is turned blue to greenish-black by alkali ; the original brown-red colour is restored by acidification.  *Reddish colour due to rosacyanine* *brown colour due to alkalinity* CO_3^{2-} in acidic medium Ferric salts also turn curcumin red-brown. However this colour , unlike that due to boric acid, does not turn blue or green on addition of alkali. This test is hindered by oxidising substances and by iodides. They must be decomposed or removed before carrying out the reaction.

CONCLUSIONS

This scheme for anion analysis needs no special equipment, instrument or reagent and may be carried out at any undergraduate or even school laboratory. The procedure has been used by undergraduate students and the results are consistent and reproducible. There has been a marked improvement in indoor air quality as no fumes were produced. A couple of years back one could find a way to our chemistry lab due to fumes of various gases and smell of H_2S, but now after the greening of these lab exercises ambience of our chemistry lab has greatly improved. The liquid waste generated is negligible and the use of LPG is almost eliminated. The scheme is relatively hazard free and is a step towards introduction of green practices to young students.

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8. Towards A Clean And Stress Free Chemistry Lab by Using Principles Of Green Chemistry – SharmaE., Bansal S., Johar P., Chowdhury S., Tucker V., Mohan R., Sidhwani. I.T.
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