Sudhangsu assay: a scratch of green chemistry for beginners

N Paul
Department of Chemistry, A.P.C.RoyGovt. College, Siliguri, West Bengal, India
E-mail: paulnabanita367@gmail.com

Abstract. Green chemistry approach is supposed to be the best attempt for saving world from the potential dangers which spread from chemistry laboratory to almost all spheres of society. In school days when budding chemists start doing hands on experiments, in most cases first scratch is done with Lassaigne’s test. The authenticity of this test in detecting special elements is unquestionable. Does this test cross hurdle, when screened through green chemistry norm? Slow generation of lethal cyanide hardly allows this test under the umbrella of Green chemistry. The current communication coined a green protocol termed Sudhangsu assay which comply with green chemistry norm for detection of special elements. Fusion described herein, takes place at a mild condition and products thereby generated, are environmentally benign molecules. In this article a green prescription for detection of special elements is compiled.

1. Introduction
Organic compounds are primarily originating from living species so composed of carbon skeleton. The unusual catenation property of carbon separates this class of compounds into different categories. The hydrocarbon part though contains carbon and hydrogen, yet element(s) other than these if present are termed hetero atom(s). Among several hetero atoms a few atoms like Nitrogen(N), Sulfur(S), Halogens(Cl, Br, I but not fluorine), Phosphorous etc are identified by easy chemical reactions. These elements are described as special elements [1]. The qualitative detection of either the presence or absence of special elements acts as a diagnostic tool for characterization of a compound. Several procedures were known but the most familiar one was Lassaigne’s test [2]. Alternative methods of detecting special elements in organic compounds had been developed, such as Middleton's test and Alkali-Sugar test. Beilstein's test offered a very quick method for preliminary detection of halogens except fluorine. In 1843, Lassaigne devised a method for detecting nitrogen present in an organic compound by fusing the compound with potassium metal. The production of potassium cyanide forced chemists to find an alternating procedure [3]. Vohl (1863) coined the use of sodium metal instead of potassium. Finally, Jacobsen replaced potassium by sodium for fusion of organic compound. In 1935, one modification of this test known as Middleton test came to be known where organic compounds were heated with zinc powder and sodium carbonate. In Middleton’s test special elements were transformed into sodium cyanide, sodium halides, sodium phosphate and zinc sulfide. Zinc sulfide was insoluble in water but dissolved in hydrochloric acid while all sodium salts were water soluble. Differential solubility of zinc sulfide from rest ionic compounds made identification process convenient. In 1937, Robertson suggested addition of small quantity of iron powder during fusion to remove sulfur. A very small quantity of iron powder was reacted with sulfur present within the investigating matter. Thus this external iron acted as a scavenger of sulfur and helped formation of considerable amount of ferrocyanide in the melt from nitrogenous compounds. All chemical
transformations were aimed to search novel methods to sustain greener part of environment. Sodium cyanide generated in Lassaigne’s test was a lethal chemical. Thus search for an alternative test was a basic target. In this context, Alkali-sugar test was considered an environmentally friendly procedure in which sucrose dust; anhydrous sodium carbonate and organic compound were mixed in the ratio 5:50:1 and fused. The extract was used for detection of special elements. Though production of lethal sodium cyanide was well controlled but the efficiency of the procedure in comparison with Lassaigne’s test was pretty debatable. Lassaigne test was an investigation which authenticated presence of special elements in organic compounds and simultaneously generated cyanide, endangered surroundings at a slow but constant rate. In order to avert potential hazards of Lassaigne test, present communication proposed a green protocol termed Sudhangsu Assay [4]. This assay introduces magnesium in lieu of sodium. Products, biproducts and residues have character of fertilizer and thereby the procedure does not face any difficulty in dealing with residue treatment. This assay satisfies green chemistry norm in almost all aspects. Being less time consuming and more environment friendly, Sudhangsu assay has the potential to exceed conventional Lassaigne test.

2. Materials and methods
Compounds taken for the study are 3-Nitrobenzaldehyde, 4-Nitrophenol, 2-Nitro aniline, 3-Nitroaniline, 4-Nitroaniline, 4-Chlorobenzoic acid, Sulfanilic acid, Sulfamic acid, urea, thiourea, 2-Phenylenediamine, m-Phenylenediamine, 1,3-Dinitrobenzene, 2-Nitrobenzoic acid, 3-Nitrobenzoic acid, 4-Bromo Acetanilide, 4-Iodoaniline, 4-Chloro aniline, Anilinium chloride, Aniliniumsulfate, Aniline, Nitrobenzene, Morpholine, 3-Amino benzoic acid, 1-Naphthyl amine, 2-Aminophenol, 3-Aminophenol, 2,4-Dinitrophenyldrazine, 2-Nitro phenol, 3-Nitro phenol, 4-Aminophenol, 4-Chloro nitrobenzene, 4-Nitrotoluene, 4-Toluidine, Anthranilic acid, 4-Anisidine, Phthalimide, Benzamide and N,N-Dimethylaminobenzaldehyde. Metal taken for fusion is magnesium and the reagents used for detection are silver nitrate, ferric chloride, ferrous carbonate, hydrochloric acid and nitric acid. All chemicals used for the assay were purchased from commercial sources with best quality. Glassware and other apparatus of ordinary quality were used for experiments.

2.1. Fusion of compounds in Sudhangsu assay
For fusion of solid compounds, in a clean mortar 50mg sample is taken and it is pressed with a pestle to get compounds in finely divided state. Now small amount (~30mg) of magnesium dust is added to the sample with a spatula and the mixture is rubbed in vigorous manner. Two are thoroughly mixed so that organic compounds get well adhered with metal dust. Entire mass is transferred to a normal size test tube and it is very gently warmed holding the test tube in inclined manner with Bunsen flame. Solid organic compounds are easily liquefied. Liquid matter often starts climbing up along the inner walls of the test tube. The test tube is removed from the Bunsen flame and liquefied matter is allowed to go down in order to bring it in contact with magnesium. If liquid does not come down, solid mass inside the tube is shaken to get adhered with outgoing liquid material. This is essential for volatile materials. Sometimes heating is done above sample level for checking escaping tendencies of organic compounds. Test tube is often shaken while warming. After warming for 3-4 minutes solid mass is left for cooling in air. However, for liquid compounds, in a normal size test tube, little magnesium dust is soaked with one to two drops of liquid sample and warmed delicately for 2-3 minutes. Test tube is often removed from the flame during heating. Fused material is used for detecting special elements. Magnesium based fire can not be doused by water. Magnesium burns in air vigorously, both nitrogen and oxygen continues ignition tendency. Sand bath must be kept ready to avoid any unwanted incident.

Detection of special elements.
First, detection of nitrogen would be covered. The solid mass is scratched with a glass rod to break any chunk. It is treated with distilled water and slightly warmed. A colourless gas comes out in feebie manner which produces dense white fumes when it comes in contact with hydrochloric acid soaked outer surface of a test tube. (Experiment is performed with very small quantity of sample, liberated
characteristic gas is thus small in amount, and hence instead of glass rod, bottom of test tube is taken for soaking it with hydrochloric acid). During detection of halogens, 1ml colourless aqueous solution collected from residual part of previous experiment is taken for investigation. One portion of aqueous part is acidified with dilute nitric acid and slightly warmed and then it is treated with silver nitrate solution. An instantaneous white precipitate appears which dissolves in ammonia solution but reappears when treated with nitric acid. This indicates presence of Chlorine. Yellowish white (or dirty yellow) precipitate, sparingly soluble in ammonium hydroxide solution indicates the presence of bromine. And, yellow precipitate almost insoluble in concentrated ammonium hydroxide solution indicates the presence of iodine. For detection of sulfur, this assay includes three tests. In first test, small portion of aqueous part (0.5ml) is added to freshly prepare dilute ferric chloride solution. Yellow colour of ferric chloride instantaneously turns blood red. This illustrates that the compound contains both sulfur and nitrogen. Thiourea responds to this test but Sulfanilic acid does not. If yellow colour of ferric chloride instantaneously turns black, it indicates presence of sulfur. Thiourea and Sulfanilic acid do not respond to this test. While in the second test, 1ml aqueous solution (colourless) is acidified with dilute hydrochloric acid, and then it is gently warmed and added to barium chloride solution. A silky white precipitate appears that dissolves in hydrochloric acid. The positive response of sulfite (SO$_3^{2-}$) radical indicates presence of sulfur in the compound. Sulfanilic acid responds to this test but Thiourea does not. In third test, 0.5ml of aqueous part is added to freshly prepare dilute ferrous carbonate solution. Solution instantaneously turns black. This illustrates that the compound contains sulfur (S).

3. Results and Discussion

The degree of covalency of Carbon-Magnesium bond plays a cameo role in the present context. Electron distribution of this bond (C$^\delta-$—Mg$^\delta^+$) though remains inclined towards more electronegative carbon yet considerable covalent character of this specific bond produces stable organo magnesium compound at an ease. Incorporation of magnesium in between carbon-hetero atom bond and subsequent polarization of the bond (C$^\delta-$—Mg$^{\delta^+-}X^{\delta^-}$) allows an easy thermal cleavage of carbon-magnesium bond. The advantage of easy to move inside and outside property of magnesium within organo family assists abstraction of special element(s) from organic compound. Fusion ultimately produces ionic compounds like magnesium nitride, magnesium halide, magnesium sulfide, magnesium sulfite, magnesium thiocyanate, magnesium phosphide etc. Identification of corresponding anionic radicals by conventional methods assists identification of these special element(s) in the supplied sample. An ordinary condition like hydrolysis is able to liberate ammonia from magnesium nitride suggesting presence of nitrogen in the compound. Silver nitrate test distinguishes different halogens. Ferric chloride test, Ferrous carbonate test and Barium chloride tests provide information on sulfur.

3.1. Chemical reactions and explanations

Alkaline earth metals have a tremendous likeliness for nitrogen. Magnesium being a member of alkaline earth family abstracts nitrogen from covalently bonded state of organic compound during thermal excitation and produces magnesium nitride which when treated with water liberates ammonia which produces dense white fumes when it comes in contact with hydrochloric acid.

![Figure 1. Reaction route for detection of Nitrogen in an organic compound.](image)

During pyrolysis, halogens of organic compound are transformed into corresponding halides and are identified by Silver nitrate test.

![Figure 2. Reaction route for detection of halogens in an organic compound.](image)
Figure 2. Chemical reaction describing identification of halogen in an organic compound.

Sulfur containing compounds combine with magnesium ion either as sulfide or as sulfite depending upon the state in which it maintains initial bonding within organic compounds. If a compound contains both sulfur and nitrogen, there remains a fair chance of thiocyanate formation. Addition of ferric ion instantaneously differentiates formation of sulfide and thiocyanate. Magnesium metal activated pyrolysis of sulphonlic acid family proceeds via breakage of C-S bond of C-SO$_3$H group. Sulfur has an extraordinary affinity with oxygen. Magnesium promotes pyrolytic elimination of sulfur trioxide. Liberated sulfur trioxide on ionization generates sulfite ion, so the extract contains magnesium sulfite which is detected using barium chloride. Sulphanilic acid, sulfamic acid gives good results to barium chloride test but thiourea does not. In case of thio urea, basic anion formed is thiocyanate ion and bariumthiocyanate is soluble in aqueous medium. When sulfur is abstracted as sulfide, black ferrous sulfide is precipitated. When sulfur and nitrogen both are present, aqueous extract often produces red rose colour of rhodanide ion with ferric ion.

$$\text{Mg(s)} + \text{C}_x\text{H}_y\text{S}_z\text{Om} \rightarrow \text{MgS} \rightarrow \text{BaS}_3$$

$$\text{Mg(s)} + \text{C}_x\text{H}_y\text{S}_z \rightarrow \text{MgS} \rightarrow \text{FeS}$$

$$\text{Mg(s)} + \text{C}_x\text{H}_y\text{S}_z\text{Nu} \rightarrow \text{Mg(SCN)}_2 \rightarrow \text{Fe(SCN)}_3$$

Figure 3. A reaction set pointing out several parallel routes for detecting sulfur.

3.2. Choice of metal in green context

Magnesium is an essential element required by both animals and plants. It is the fourth most abundant element found in human body and it plays a central role in chlorophyll activation. Its role in photosynthesis and its action as a cofactor in many biochemical reactions are granted features. Though magnesium dust which is directly used in the current assay does not exhibit these biochemical characteristics but it is the same element in a different state that gets incorporated into human and plant cycle to perform these activities. Magnesium has almost no report to undergo vast changes from the basic form when left exposed to environment. Magnesium dust is less toxic and so it is non-hazardous to health. Moreover, this metal is neither carcinogenic nor mutagenic [5]. The most significant achievement in Sudhangsu assay is prevention of lethal cyanide formation. Fatal cyanide poisoning happens to take place by inhalation, ingestion, absorption through skin, eyes, and ears. Moreover, cyanide has an affinity with methemoglobin and their combination produces cyanomethemoglobin. Cyanide is toxic even at very low concentration. On disposal to environment it also vitiates aquatic lives. On the contrary, human beings are less affected by exposure to magnesium oxide fumes which is likely to come out during fusion of organic compounds. In the green environment scale (0-3), magnesium oxide fume scores 0.8 where score 3 denotes highly hazardous state [6]. Thiocyanate developed from compounds containing both nitrogen and sulfur is seven times less toxic than cyanide [7]. Moreover, thiocyanate being a human metabolite is found inside body, chances of thiocyanate poisoning during experiment is low. In the current assay, use of magnesium produces environmentally friendly magnesium nitride instead of cyanide and thereby offers green route for special element detection.

3.3. Advantage of this assay over conventional methods
Sudhangsu assay in comparison with Lassaigne’s test exceeds on following facts. First and foremost it prevents formation of lethal cyanide. Fusion is carried out at milder condition. Handling of magnesium is more comfortable than sodium. Reagents used in Sudhangsu Assay are more environmentally friendly than Lassaigne’s prescription. Experimental condition is less vigorous and always follows laboratory safety norms. In presence of sulfur, nitrogen detection does not experience any interference. Residual matters and biproducts of this assay have environmentally benign features. No crushing of fused material is required so the current test does not produce any broken glass wastage. In short experimental technique of Sudhangsu assay appears straight forward.

3.4. A comparative study of Lassaigne’s test and Sudhangsu assay

In this section, a comparative study is carried out between Lassaigne’s test and Sudhangsu assay graphically. Both procedures are related to qualitative test, so pie charts are likely to represent their positive response towards detection of special elements and their attachment with green chemistry norm in comparative ground.

![Figure 4](image)

**Figure 4.** Comparative graphical statement about nitrogen detection by two protocols.

Figure 4, illustrates Sudhangsu assay records little higher positive response towards nitrogen detection than that is found in Lassaigne’s test. Incomplete fusion of sulfur containing nitrogenous compounds is often responsible for missing nitrogen in Lassaigne’s test while this scope does not arise in Sudhangsu assay since nitrogen has an extraordinary affinity with magnesium. Moreover, Sudhangsu assay is complied with green chemistry. Figure 5, demonstrates detection of halogen maintains almost same status in terms of positive response. But two protocols show little difference when looked thorough green context. Reagents used for detection of halogen are same in both tests; the only difference is noticed with method of fusion. Sudhangsu assay is associated with milder fusion method so maintains a small degree of green character.
Both protocols again record equal ability towards positive response during sulfur detection. Sudhangsu assay however prefers to stick with green approach to a significant extent by choosing environment friendly reagents as much as possible. Figure 6, however points out entire procedure associated to sulfur detection in Sudhangsu assay cannot be considered green. When existing sulfur transformed into sulfite, barium chloride is incorporated as investigating agent and that part is likely to fall in the domain of conventional approach.

3.5. Impact of residue on environment
The strategy of a green route is not only to focus on prime products but also to throw light on biproducts and on relevancy of different chemicals involved in the particular change over. Maintenance of green environment is essential inside laboratory. Proper care should be taken for disposal of laboratory wastages. This assay takes care of generating typical residues which when
exposed to environment does an advantage to surroundings. Residue of this assay has characteristics of fertilizers. This assay does not produce broken glass wastage during extract preparation. Guidelines for magnesium content in drinking water are not rigorous. WHO guidelines for drinking water suggest that drinking water containing magnesium has been connected with numerous health benefits. According to guidelines prescribed by WHO, magnesium metal in water maintains blood pressure, eases up muscle movement including cardiac muscles, and even prevents atherosclerosis giving a cardiac patient maximum benefits [8]. It activates many enzymes required for plant growth. Magnesium hydroxide dissolves in water at a rate of 12mg/L. Magnesium is absent in rain water and river water unless it is very hard. The input of magnesium from soil to human via food chain does not pose any threat. Magnesium nitride is a convenient source of ammonia. If residue moves to soil, hydrolysis liberates ammonia which enriches nitrogen content of soil. This is supposed to be fastest way to release nitrogen and magnesium to soil. Magnesium sulfite has a better solubility in soil water. Residue if contains magnesium sulfite, on aerial oxidation acquires characteristics of Epsom salt, a good quality fertilizer. Sulfites are useful to check bacterial and fungal growth thereby preventing eutrophication. Sulfur is an essential element for plant. It thwarts diseases in plants and promotes its growth. In short waste disposal scheme associated with Sudhangsu assay sounds sensible.

4. Conclusion
Lassaigne’s test is a proven test if one looks into the matter from chemistry perspective. Searching for an alternative finds almost no logic. But chemistry is a benign subject for all fields, so when the test is judged through the eye of an environmentalist it underscores. In this circumstance a search for alternative route seems judicious. Keeping prime objective of checking generation of cyanide and its subsequent spread out in environment, alkaline earth metal magnesium is introduced in place of alkali metal sodium. This introduction channelizes the thermal pyrolysis through generation of nitride and liberating ammonia on hydrolysis. Nature of halogen detection scheme resembles Lassaigne’s prescription but regarding sulfur this assay avoids non-environmentally favourable chemical like lead acetate by performing ferric chloride, ferrous carbonate and barium chloride tests. Thiocyanate radical is formed easily and its instantaneous response towards ferric chloride detects nitrogen and sulfur together. In short, a slight modification of the conventional test as introduced in Sudhangsu assay helps budding chemists to hail green campaign inside chemistry laboratory.

5. References
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