GREEN ANALYTICAL CHEMISTRY

Article Review

Hana Sh. Mahmood
Department of Chemistry/College of Science, University of Mosul/Mosul /Iraq
Email: hnsheker@yahoo.com

ABSTRACT

Nowadays, the most important development concept in analytical chemistry is the modified version of green analysis and environmentally friendly approach; some of these concepts are the selection of safer procedures, solvents, and techniques as well as the use of analytical procedures that generate less hazardous waste. The basic requirements of many chemical procedures are the use of solvents for dissolution, extraction, purification, carrier or mobile phase and other specific uses as spectral properties enhancements. on other hand, chemical indicators, oxidants and colour development reagents consider the basic requirements of many analysis procedures use. This is a review of green and friendly environmental procedures, reagents, solvents, and techniques used for analytical determinations of different analytes.

KEY WORDS: green chemistry, friendly environmental, solvents, techniques

ملخص

في الوقت الحاضر، يعد التطوير الأكثر أهمية في الكيمياء التحليلية هو التحليل باستخدام الكيمياء الخضراء والنهج الصديق للبيئة، والذي يشمل اختيار الكواشف والمذيبات والتقنيات الأكثر أمنا على صحة الانسان والمجتمع وعلى ديمومة البيئة بالإضافة إلى استخدام التحليلات التي تولد اقل ما ممكن من المخلفات. المبدأ الأساسي للعديد من الإجراءات الكيميائية هو استخدام المذيبات للإذابة أو الاستخلاص أو التنقية كما انها تستخدم كطور متحرك في التحاليل الكروماتوغرافيا او كطور ناقل ولها بعض الاستخدامات التخصصية مثل تحسين الصفات الطيفية لبعض المركبات. من جانب اخر، تعتبر الكواشف الكيميائية والعوامل المؤكسدة وكواشف تكوين الصبغة من المتطلبات الأساسية للعديد من التحليلات الكيميائية. هذه مراجعه اتناول فيها العديد من الطرائق التحليلية التي تتضمن اتباع طريقة عمل امنة وكواشف ومذيبات صديقه للبيئة وكذلك عرض للتقنيات التحليلية التي تصل الى حدود كميه واطئة لعينات النموذج وبالتالي تختزل مخلفات التحليل.

INTRODUCTION

Green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and the generation of substances hazardous to human health and the environment.

Substances that are toxic to humans, the biosphere and all that sustains it, are currently still being released at a cost of life, health and sustainability. One of the green chemistry's greatest strengths is the ability to design for a reduced hazard.

The goal of green analytical chemistry is to use safe analytical procedures that generate less hazardous waste and as well as developing the old methods to incorporate procedures that either use less hazardous, smaller amount, precise automated techniques.

The First Topic - Classification of Chemicals

The word "Green" has been created by Massachusetts Institute of Technology which classify chemicals according to their hazardous effect on humans and environment to different classes:

1. Flammable Liquids
2. Corrosive Chemicals
3. Explosive Chemicals
4. Toxic Chemicals
5. Compressed Gases
6. Carcinogenic Chemicals

Flammable liquids are volatile i.e. is a liquid that has a flash point of less than 37.8oC, like acetone, ethanol, and xylene, the vapor of some of these flammable chemicals, not the liquid, are often heavier than air, and tend to settle such as ethyl ether, isopropyl ether, tetrahydrofuran, can lead to health hazards - skin reactions and inhalation illnesses. (never be stored with oxidizing agents, e.g., nitric, perchloric and sulfuric acids

Corrosive Chemicals these include concentrated acids and bases. The fumes of concentrated corrosives can cause severe external and internal burns.

Explosive Chemicals acids like picric acid is more sensitive explosive than T.N.T. it always stored in water and have to be kept out of contact with metals as much as possible. Ethyl Ether is a highly volatile and flammable solvent requiring special storage and disposal procedures. With exposure to air, peroxides will form. When the peroxides are concentrated by evaporation of the ether, an explosion will occur. Isopropyl ether and other ethers also form peroxides readily. Ethyl Ether is preferably obtained in metal cans.

Toxic Chemicals are commonly used in the laboratory. One example of a toxic chemical used in the laboratory is epoxy catalysts containing isocyanate compounds. Acids react with cyanides to produce hydrocyanic acid its vapor is potentially lethal. Mercury is extremely toxic and should be stored in plastic, air-tight containers, away from direct heat or sunlight, and at as low an ambient temperature as possible.

A compressed gas is defined as a gas having pressure in the container of 40 psi or greater at 70oC., Any flammable liquid having vapor pressure exceeding 40 psi at 38oC is also classified as a compressed gas. e.g. carbon dioxide, propane, and ammonia.

Carcinogenic compounds include a big list of chemicals 2-Acetylaminofluorene, Acrylonitrile,4-Aminodiphenyl, Asbestos, Benzene, Benzidine, Bis-chloromethyl ether,1,2-Dibromo-3-chloropropane, 3,3'-Dichlorobenzidine (+ salts),4-Dimethylaminoazobenzene,Ethylene oxide, Ethyleneimine, Inorganic arsenic Methyl, chloromethyl ether, a- Naphthylamine, b- Naphthylamine,4-Nitrobiphenyl ,N-Nitroso di -methylamine, B-Propiolactone, Vinyl chloride, Adriamycin ,Afltoxins,2-Aminoanthraquinone, o-Aminoazotoluene,1-Amino-2-methylanthraquinone Amitrole, o-Anisidine hydrochloride, Benzotrichloride, Beryllium ,Bischloroethyl nitrosourea,1,3 Butadiene, Cadmium and some compounds, Carbon tetrachloride, Chlorendic acid, Chlorinated paraffins ,Chloroform,CCNU,3-Chloro-2-methylpropene,4-Chloro-o-phenylenediamine,C.I. Basic red 9 mono HCl, p-Cresidine ,Cupferron, Dacarbazine, DDT, 2,4-Diaminoanisole sulfate,2,4 Diaminotoluene and more than 60 proved carcinogenic compounds including some drugs at cetrain dose such as Analgesics with Phenacetin.

The Second Topic -Solvents

Analytical chemical procedures include the use of solvents for different purposes as dissolution, Extraction, Purification. In addition, they are used in analytical chemistry as Carrier or m.ph.,Specific uses (spectral properties) as it used for the dissolution ,and extraction, while it is used in Industrial pharmacy as diluent for example D10 (dextrose 10%), D5 (dextrose 5%), NS (normal saline) (which are considered solutions not solvents).Organic solvents are used in very low concentrations 0.1% or less (propylene glycol, polyethylene glycols, ethanol), solvents described in specific applications (dimethyl sulfoxide, N-methyl-2-pyrrolidone, glycerol) and solvents reported in other applications ethyl lactate .

Water is consider the only one green solvent while ethanol, methanol, acetone, propanol, ethyl acetate, and ethylene glycol may be considered as friendly environment solvents with respect to toluene, cyclohexane and acetonitrile. However; while solvents like dioxin, benzene, and carbon tetrachloride are more toxic and undesirable. The original solvent selection guide was published in 1998 assessed the use of 47 solvents in chemical reactions considering recycling, environmental impact, health and flammability issues amongst others.

The Third Topic- The Use of Greener Reaction Conditions

Redesign of reaction procedure: This includes the replace of the hazardous solvents with a lesser impact solvent on the human health and the environment, or the design of solventless reaction conditions or solid-state reactions, use novel processing methods that prevent pollution at its source, and eliminate energy- or material-intensive separation and purification steps, improve energy efficiency, including reactions running closer to ambient conditions.

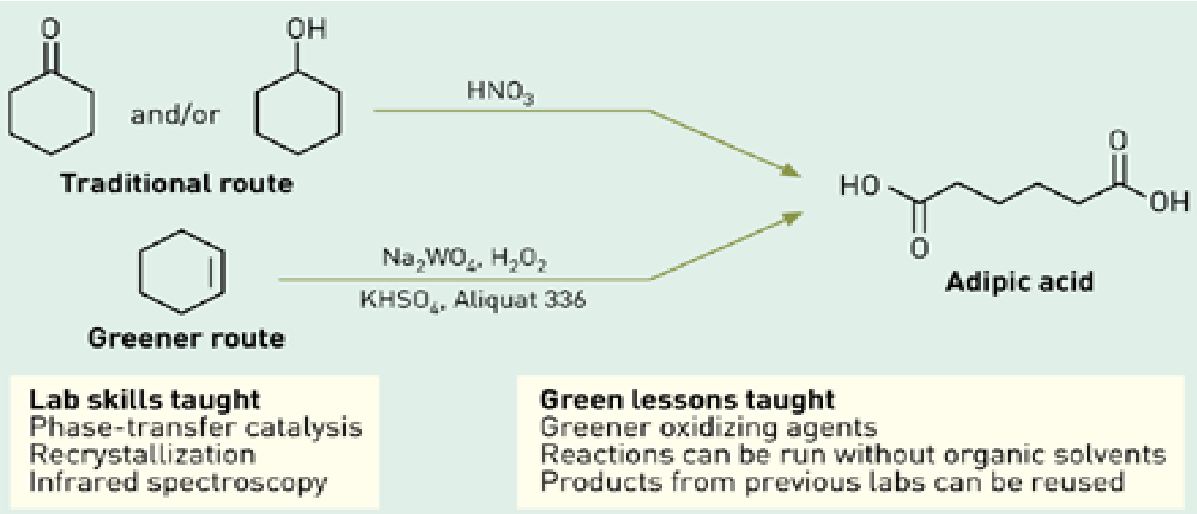

Figure 1. redesign of reaction procedure

Kazuhiko Sato, Masao Aoki, Ryoji Noyori, A "Green" Route to Adipic Acid: Direct Oxidation of Cyclohexenes with 30 Percent Hydrogen Peroxide, Science11 Sep 1998 : 1646-1647.

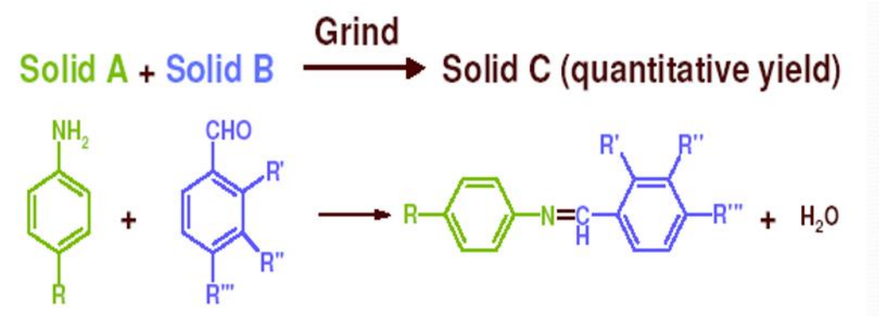

Figure 2. Solid-State Reactions

Automation: other tool to produce greener reaction conditions is automation which improves measurements by fast sampling, fast analytical control of the baseline/background, an easy and rapid standardization, improved repeatability, a considerable reduction of reagent, solvent consumption, and waste generation, and a possible enhancement of the analytical sensitivity through the online coupling of detection with preconcentration/separation techniques

Replacement of reagent: the determination using the pharmaceutical compounds as reagent for color development in colorimetric method is consider a new way to design greener reaction; as an example, determination of paracetamol using the pharmaceutical compound naproxen instead of chemical reagent in which it is used as a coupling agent for the diazotized p-aminophenol (the hydrolysis product of paracetamol). The paper offers a determination of an analgesic paracetamol in the presence of high content of another analgesic, as well as eliminate the requirements to chemical hazard reagents.

Replacement of oxidant: oxidizing agent (oxidant, oxidizer) is a substance that has the ability to oxidize other substances, in other words to accept their electrons. Common oxidizing agents are oxygen, hydrogen peroxide, potassium permanganate, potassium chromate, and potassium periodate.

Potassium permanganate is safe even at large concentration. It is rare toxic; chromate is carcinogen, highly toxic by inhalation, toxic by skin absorption, corrosive, and Mutagen in the same manner potassium periodate is corrosive, acute toxic, health hazard, irritant, and environmental hazard.

Potassium permanganate was used for determination of Famotidine in both pure form and in its dosage forms via oxidation of the drug in acid or alkaline media and was used for oxidation of the synthesized hydroxy analog of Naproxen at two different medium acidic and basic.

Solvent Reduction and Replacement: A green uv spectrophotometric method is used for determination of paracetamol and tramadol in the presence of each other in dosage form, the method is based on dissolving of 25 microgram of the sample in milliliter of water, estimating the quantity of paracetamol at two wavelengths 242 nm and 227 nm where tramadol exhibits the maximum absorption as shown in figure 3:

By the application the equation of multi component system as below:

$$A \text{ (paracetamol) at 242 nm} = \varepsilon bc \text{ at 242 nm}$$

Where A is the absorbance, ε is the molar absorptivity, b is the cell thickness (1 cm) , and c is the molar concentration

$$A \text{ at 227 nm} = \varepsilon bc \text{ of paracetamol at 227 nm} + \varepsilon bc \text{ of tramadol at 227 nm}$$

C (tramadol) at 227 nm=[A- (εc)of paracetamol at 227 nm]/[ε of tramadol at 227 nm.]

This procedure eliminates the role of organic reagent and organic solvent and already reduce the waste.

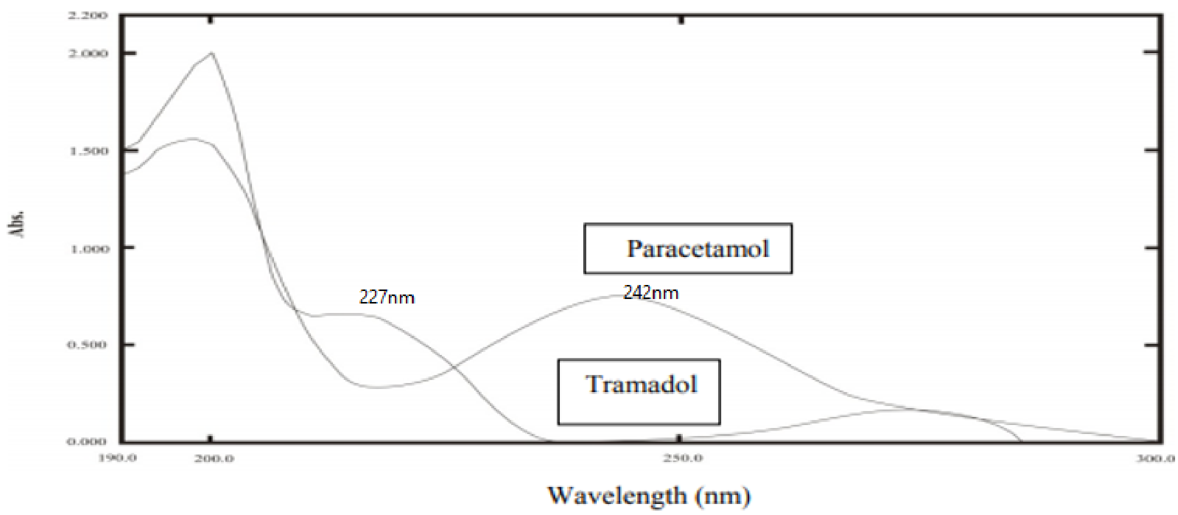

Figure 3. Absorption spectrum of 25 µg/ml of paracetamol (242 nm) and tramadol hydrochloride (227 nm)

Hana Sh. Mahmood, & T. Dawood, N. (2018). Determination of paracetamol and Tramadol hydrochloride in pharmaceutical preparations using green UV method. Rafidain Journal of Science, 27(1), 36-42. https://doi.org/10.33899/rjs.2018.141184

In other side paracetamol has been determined but with maximize procedure and harmful reagents like nitroaniline (hemolysis compound).The irritant thymol was also used as a coupling agent for determination of paracetamol in alkaline medium and irritant hexacyanoferrate was used for determination of paracetamol as an oxidant in the presence of ammonia, the skin inflammatory compound phloroacetophenone was used as a coupling compound to determine paracetamol in basic medium. Dichlorodicyano benzoquinone which produces the toxic CN in water was used for determination of paracetamol via charge transfer reaction.

The Fourth Topic- Friendly Environment extraction techniques:

Many analytical procedures require extraction steps before determination step to separate the analyte from other interfering compounds or impurities. The ordinary extraction techniques consume solvents and time.

The methods classified below reduce the use of organic solvents and speed extraction times compared to traditional liquid-liquid extractions.

Accelerated solvent extraction (ASE)

Ultrasound extraction

Microwave assisted extraction (MAE)

Supercritical fluid extraction (SFE)

Membrane extraction

Liquid-solid extractions

Cloud Point Extraction (CPE)

Accelerated solvent extraction (ASE) uses pressure and heat (up to 200 °C) to speed extractions, and decrease the volume of solvent to 1.2-1.5 times less than that of the ordinary solvent extraction.

Ultrasonic extraction uses high frequency acoustic waves to create microscopic bubbles in liquids. The collapse of the small bubbles produces small shock waves, cavitation, that are particularly well suited for breaking up or promoting the dissolution of solids. Ultrasonic extraction has been applied to a variety of organic extractions. These include the extraction of nicotine from pharmaceutical samples into heptane for GC analysis, phthalates from cosmetics which reduced the amount of solvent required compared to the conventional method. Ultrasound has also been used for inorganic analytes, most recently to extract mercury into aqua regia from milk samples.

Microwave-assisted extraction (MAE) is the process of using microwave energy to heat solvents in contact with a sample in order to partition analytes from the sample matrix into the solvent which is reduced to less quantity of about (0.5-5 ml) such as the extraction of polycyclic aromatic hydrocarbons (PAH) from soil and pesticide residues from plant materials as well as extraction of organic and organometallic compounds from a wide variety of matrices with lesser waste.

Supercritical Fluid Extraction (SFE) and Superheated Water Extraction (SWE).

A critical point (or critical state) is the end point of a phase equilibrium curve like the liquid–vapor critical point, the end point of the pressure–temperature curve that designates conditions under which a liquid and its vapor can coexist. Solvents that are heated and pressurized above their critical point, exhibit properties intermediate between those of liquids and gases, making them ideal for separations and extractions. Many SFEs are performed with carbon dioxide (SFE-CO2), which has a readily accessible critical point (31.1 °C, 74.8 atm) along with being inflammable and nontoxic. The efficiency of SFEs is affected by the choice of extraction solvent as well as the extraction pressure, temperature, filler materials (mixed with the sample matrix), modifiers (cosolvents), and collection solvent. The challenge of SFE-CO2 is the very low solubility of polar materials.

Membranes are selective barriers between phases, provide an alternative for green analyte isolation and preconcentration. There are two primary membrane techniques, filtration and extraction. Membrane filtration uses porous membranes to separate solution components based on size using a pressure difference between the donor and acceptor solutions as the driving force, whereas Membrane extraction primarily exploits concentration gradients using nonporous membranes.

Liquid-solid extractions involve the eliminate of solvents in the pretreatment process because the analyte can be directly extracted from the liquid sample onto solid sorbent material. The availability of different materials is one of the advantages of sorptive techniques. The technique was applied for extraction of pesticides, steroids, fatty acids, and drugs.

Cloud Point Extraction (CPE).

Aqueous solutions of non-ionic surfactants (Triton x-100 and tween-80) become turbid when they are heated above the temperature known as the cloud point. The solution is then separated into two isotropic phases, i.e. a surfactant-rich phase and a bulk aqueous phase. The hydrophobic solutes and metal ions, after the formation of sparingly water-soluble complex, can be enriched into the surfactant-rich phase. (In liquids), the cloud point is the temperature below which a transparent solution undergoes either a liquid-liquid phase separation to form an emulsion or a liquid-solid phase transition to form either a stable sol or a suspension that settles a precipitate. A cloud point extraction (CPE) less commonly used extraction, where the metals are extracted into micelles with a complexing agent in the presence of a surfactant.

The Fifth Topic -Green Techniques

Technologies that meet the scope and then be judged on how well they meet the criteria including science and innovation (original), human health and environmental benefits (reduce toxicity, reduce hazard materials ,..), applicability and impact by used on wide range for samples.

Spectroscopy especially infrared, Raman, and x-ray diffraction are rather green technique in which sample sizes are small, and need not to sample preparation.

Atomic absorption spectrometry (AAS) detects elements in either liquid or solid samples through the application of characteristic wavelengths of electromagnetic radiation from a light source. AAS reduces the required sample volume and need not reagents.

Flow Injection offers the combination of injection of a well-defined volume of sample, precise timing (from the point of injection to the point of detection) (controllable dispersion), and reproducible readout of the recorded signal. Determination of lead with Arsenazo III and phenol in water by oxidative coupling to 4-aminoantipyrine in the presence of hexacyanoferrate (III). procedures employ continuous, unidirectional pumping of carrier and reagent streams, which uses programmable, bidirectional discontinuous flow as precisely coordinated and controlled by a computer exhibits the ability of performing different determinations without system reconfiguration.

Electrochemistry is a unique area of analytical chemistry where sample treatment has historically been relatively green but a hazard has come in the form of the mercury working electrode. A developing modified carbon as the basis for working electrodes instead of dropping mercury electrode, and the use of new ion selective electrodes was big transformation to green sensors.

Bioanalytical methods are often green due to the highly selective nature of the reactions, which usually removed the need for further separations or concentration steps, improving the greenness of the methods. A novel bioanalytical techniques include an enzyme-linked immunosorbent assay (ELISA) .

Conclusion

Green chemistry is not a solution to all environmental problems but it is the most fundamental approach. As we are earlier starting changes toward green since it offers more solutions to our health and environments.

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