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ANALYTICAL METHOD FOR THE DETECTION AND QUANTIFICATION OF IMPURITIES PRESENT IN CANE SUGAR BY USING ICP OES METHOD

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ABSTRACT

Raw sugar and Jaggery has been currently used by people all over Tamilnadu instead of white sugar because of low fatty content and health. Some of the impurities (Metals)like sodium bicarbonate, Sodium hydro sulphite, Super phosphate were added in the production of raw sugar and jaggery to increase the colour, taste and quantity. These metals are added, principally to increase the acceptance of the product, by the customer. To ensure food safety, it is also essential to develop effective and reliable analytical methods for the monitoring of the additive levels in food. Therefore a new method called ICP-OES was developed and validated for the quantification of impurities present in raw sugar and jaggery.

ICP-OES was performed out on Shimadzu and Microwave Digester-Multiwave Pro or Hot Plate using Suprapure 3% conc. HNO_3. From the results, we conclude that all the elements/ metals like sodium bicarbonate, sodium hydrosulphite and supper phosphate exceeds the limit as per FSSAI. The results of validation parameter- linearity was found to be in the range of 1, 10&50 ppm and was found to be 0.995 and 0.999. Other parameters such as Accuracy, Repeatability, Reproducibility, Limit of Detection and Limit of Quantification were was found to be within the limit as per ICH guidelines Q_2R_1. Analysis of raw sugar and jaggery sample by the developed ICP-OES methods shows the amount of impurities in the sample were exceeding the limit.

KEY WORDS: Jaggery, Raw Sugar, Impurities.

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INTRODUCTION

Food analysis is the discipline dealing with the development, application and study of analytical procedures for characterizing the properties of foods and their constituents. These analytical procedures are used to provide information about a wide variety of different characteristics of foods, including their composition, structure, physicochemical properties and sensory attributes. This information is critical to our rational understanding of the factors that determine the properties of foods, as well as to our ability to economically produce foods that are consistently safe, nutritious and desirable and for consumers to make informed choices about their diet.

IMPORTANCE OF FOOD ANALYSIS

Any product that is going to be used by humans needs to be rigorously tested, and because foodstuffs are ingested, the testing is often more crucible to avoid any health issue from occurring. If a company produces bad foodstuffs, then the consumer can not only get ill, but it can also cost them a lot of money in lawsuits and in reputation (the latter of which often has worse long-term implications compared to short-term financial losses). So, ensuring that foodstuffs contain what they are meant to (in the ratios they are meant to) is crucial and can be performed either in house or at a contract analysis/research institute.[2]There are many reasons why companies want to analyze foodstuffs, and there are quite a few general areas of food analysis. In terms of the techniques that are used, the go to choices are a wide range of analytical characterization instruments that are found in almost all quality control laboratories. For food analyses, the range of instruments used includes nuclear magnetic resonance (NMR) spectroscopy, gas chromatography(GC), atomic absorption spectroscopy (AAS), and high performance liquid chromatography (HPLC), flame photometry and inductively coupled plasma atomic emission spectroscopy (ICP-AES) to name a few common examples. Methods which are more 'wet chemical' in nature, such as titrations and thin layer chromatography(TLC), can also be used. The choice of techniques varies depending on what foodstuff is being analyzed, what is being analyzed within the foodstuff, and what the reasons for the analysis is.

FOOD ADULTERATION

Economically motivated food adulteration or food fraud is currently recognized as a great threat to public health. The public health related aspect of food adulteration is the matter of academic study. A specialized database in this field is expected to encourage objective research for development of strategies that may prevent the occurrence of food fraud in the days to come. Almost all food is reported to be subjected to food adulteration including dairy products, fish, seafood, honey, oils, grains, alcoholic beverages, infant formula, etc. It is high time to shift the focus of addressing this problem from intervention to prevention. Food fraud and food contamination are different. Food contamination may happen as a natural consequence of a process. Food fraud is generally done for some economic gain. The malpractice is attempted to be controlled by systematic governance since the last century.

Food adulteration refers to the process by which the quality or the nature of the given food is reduced through addition of adulterants or removal of vital substances. It is a widely occurring phenomenon practiced throughout the globe and has attracted the attention of the community since the last century Food adulteration refers to the foreign and usually inferior chemical substances present in food that cause harm or is unwanted in the food. Basically, food adulterations, small quantities of the non nutritious substances are added intentionally to improve the appearance, texture or storage properties of the food. Food adulteration is quite common in the developing countries.

TYPES OF FOOD ADULTERATION :

Intentional adulteration :

The adulterants are added as a deliberate act with intention to increase profit.Example: sand, stones, chalk powder and marble chips.etc

Incidental adulteration:

Adulterants are found in food due to negligence, ignorance or lack of proper facilities.Example: packaging hazards like larvae of insects, droppings, pesticide residues, etc.

Metallic adulteration:

When the metallic substances are added intentionally or accidently.Example: arsenic, pesticides, lead from water, metals, mercury from effluents, tins from cans, etc.

ADULTERATION OF FOOD STUFFS

Table 1: Adulteration of food stuffs

Food stuffs	Adulterants
Cereal	Soil, pieces of stone, intested cereal
Bengal gram flour	Starch powder, maize flour
Ghee	Vegetable ghee, animal fat, sweet potato
Milk	Water
Tea	Used tea leaves
Pepper	Papaya seeds
Clove	Clove after extraction
Dhaneya	Saw dust, horse dung
Red chilli powder	Saw dust red powdered bricks
Honey	Sugar, water
Turmeric	Yellow soil, metanil yellow

Fig 1: Types of sugars

PRODUCTION

India is the largest producer of sugarcane next to Brazil and this crop is cultivated underdiverse situation in India.India ranks second (Brazil comes first)in sugar production and consumption. India's production is expected to rise to 24.5 million tonne although the annual demand is 22 million tonne. Sugar producing states are Uttar Pradesh (24%), Maharashtra (20%), Gujarat, Tamil Nadu, Karnataka and Andhra Pradesh. There are 453 sugar mills in India of which 252 are co-operatives, 134 are private, and 67 are public sector mills.[1]

Brazil was the single largest producer with 29.93million metric tons of sugar produced in 2019-2020. In the 2019-2020 crop year, global sugar production was approximately 166.18 million metric tons, with 182 million metric tons expected for 2020-2021. Approximately 80% of the world sugar is produced from sugar cane is tropical and subtropical climates. The remaining 20% comes from sugar beets, which are grown mostly in the temperatezones of the northern hemisphere. A total of over 120 countries produce sugar.

The largest sugar producing counties were as follows:

1. BRAZIL – Brazil regained its historical places as the world largest sugar producer from india during 2019-2020 crop year. The country produced 29.93

million metric tons of sugar.Furthermore,the U.S department of agriculture (USDA) forecasts that brazil sugar production will increase by over 40% to more than 42 million tons during 2020-2021.This massive increase in sugar production will be achieved by shifting a substantial fraction of brazil sugar cane crop from ethanol production to sugar production. In addition to being the worldslargest sugar producer, brazil is second only to the united states in ethanol production. Since the mid-1990s, the volume of sugar cane harvested and processed in brazil has almost tripled. That reflects the rising demand for sugar cane ethanol and renewable fuels in general .with no drop in food production over the time, brazil has proved its viability as an effective and efficient powerhouse.

2.INDIA– India fell back to second place in sugar production during 2019-2020, narrowly losing the top spot to brazil. India's economy produced 28.9 million metric tons of sugar. That is about 17% of the world total sugar production of 166.18 million metric tons. India's sugar production is down from 2018-2019. However the country expects sugar production to rise by 17% for 2020-2021. What is more, domestic consumption of sugar in India in forecast to hit a new record of 28.5 million tons.Sugar derived from sugarcane in these refineries of India is vegan. Filtration and declourisation techniques for cane sugar can involve either bone char, traditional granular / activated carbon (coal, wood, coconut), or the use of synthetic ion exchange resins. Manufacturers of cane sugar in India use the latter or sulphur dioxide.

It forms the basis for many important industries like Gur, molasses,alcohol, sugar beverages, chipboard, paper, confectionery and provide raw materials tomainly other industries such as chemicals, plastics, paints, synthetics, fibre, insecticides,detergents. A wide range of industries consume sugar as a raw material. The dairy processing industry consumes an estimated 1.27 million MT of sugar consumption, accounting for 24 percent of the total industrial consumption. Confectionary, bakery and carbonated beverages are the other leading sugar consumers that account for an estimated 19 percent, 15 percent and 15 percent share, respectively.

Sugarcane is primarily grown in nine states of India: Andhra Pradesh, Bihar, Gujarat, Haryana, Karnataka, Maharashtra, Punjab, Uttar Pradesh and Tamil Nadu. More than 50 million farmers and their families are dependent on sugarcane for their livelihood. The sugar industry caters to an estimated 12 percent of rural population in these nine states through direct and indirect employment. Effectively, each farmer 19 contributes to the production of 2.9 MT of sugar every year.

The area under sugarcane rose from 1.47 million hectares in19543-1950 to 4.08million hectares in 1998-99 before declining to 2.995 million hectares in 2003-04 at all India level. The production of cane also increased accordingly from 50.14 million tones to 293.73million tons before declining to 230.18 million tons, respectively, in the above periods.

According to the latest reports by Indian Sugar Mills Association (ISMA),sugar mills across the country have produced 303.6 lac tons of sugar between 1st October 2020 and 15th may 2021. This is about 38.28 lac tons higher than 265.32 lac tons produced at the same time last year. However as compared to 63 mills which were crushing sugarcane on 15th may 2020,44 sugar mills are crushing sugarcane on 15thmay 2021 this year.

On 16 December 2020, the cabinet committee on economic affairs (CCEA) approved assistance of about Rs.3,500 Crore towards sugar export for the sugar season 2020-2021 to curtail sugar glut situation in India and to reduce the quantum of sugarcane arrears owed by the sugar industry. The subsidy aims at covering expenses on marketing costs including handling, upgrading and other processing costs and costs of international and internal transport and freight charges on export of up to 6 million tonnes of sugar limited to Maximum Admissible Export Quota(MADQ)allocated to sugar millsfor sugar season 2020-2021. During the previous season, export subsidy about Rs.6,268crore was announced by the government.

However, the average productivity of sugarcane has increased from 34.13 tons to78.86million hectares. Sugar and its by-products play a pivotal role in agriculture and agro-industrialeconomy and contributed to nearly two percent of GDP(Gross Domestic Product).

The Indian sugar consumption has steadily increased at 3.5 percent since 1996. Typically, sugar consumption is driven by the GDP growth and this has been the case for India as well. The per capita

consumption has seen a steady growth of 2.1 percent CAGR over this period, while the population has grown at a CAGR of 1.4 percent.

The evapotranspirationof sugarcane is estimated at 8–12 mm/tons ofcane and the total rainfall required by sugarcane is estimated to be 1500–2500 mm/year, which should be uniformly spread across the growing cycle.In India more than 61 percent of the cane is used for white sugar extraction and 26.5 percent is diverted for manufacture of Gurandkandsarisugar.
Tamil Nadu is one of the major canegrowing states in India, contributing 6.41 per cent of national cane and producing 7.64 percent national cane production in 2013-2021

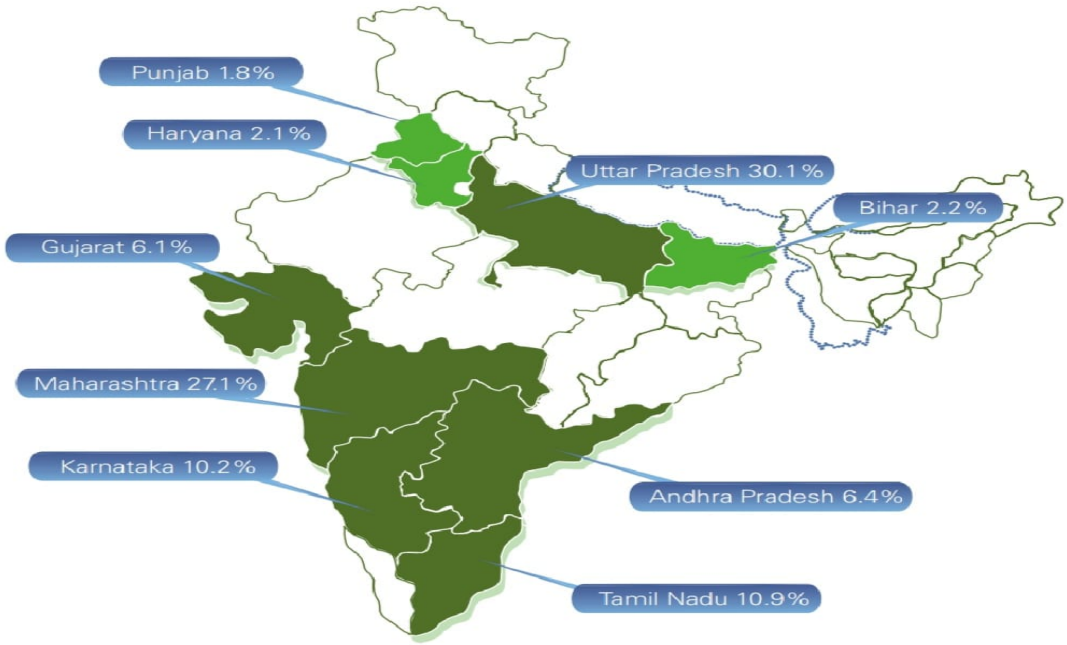

Fig 2 : Sugarcane Production of India

SUGARCANE PRODUCTIVITY AND SUGARRECOVERY ZONES IN INDIA

Table 2:*Sugarcane productivity*

High (>70t\ha)	TamilNadu, Maharastra, Gujarat, Karnataka, Andhra Pradesh, Haryana, Punjab
Medium(50-70t\ha)	UttarPradesh, Uttaranchal , Orissa, West Bengal, Kerala
Low (<50t\ha)	Bihar, Madhya Pradesh, Rajasthan, Assam

Table 3: Sugar Recovery Zones:

High (>10%)	Maharastra , Gujarat , Karnataka
Medium (9-10%)	Uttar Pradesh, Uttaranchal, Andhra Pradesh, Haryana, Punjab, Madhya Pradesh
Low (<9%)	West Bengal, Assam , Kerala, Orissa, Tamil Nadu

SUGAR TYPES :

Sugar/Sucrose can be produced from sugarcane, sugar beet, sweet sorghum, palm/coconut, sago, maple, corn, barley, grapes, dates, agave, and from honey and milk as well. The major categories of sugar produced worldwide are granulated, brown, liquid and invert sugar

- Raw Sugar/Pure Sucrose/Natural Brown Sugar
- Jaggery/Gur/Khandsari
- Invert Sugar
- Palm/Coconut/Coco Sugar

SOME DIFFERENT SUGARS:

Agave nectar / syrup, bakers special, barley sugar, brown sugar (light & dark) / free flowing brown sugar / turbinado sugar / date sugar / Demerara/ demerera sugar / Muscovado sugar / Barbados sugar, brown rice malt syrup, candy sugar, castor sugar, coarse sugar, coconut sugar, confectioners / powdered sugar, corn sugar, corn sugar, corn starch / syrup, cube sugar, dextrose, flavoured sugars (like cinnamon & coffee), fructose / foot sugars, fruit sugar, galactose, granulated sugar, golden syrup / cane syrup / kakvi, glucose, invert sugar, inverted sugar syrup / treacle / molasses, juice / sucanat, lactose/ milk sugar, liquid sugar,maltose, mannitol / manna sugar / mannite,maple sugar, maple sugar, organic sugar,palm / coconut / arenga sugar, regular sugar / fine / extra fine sugar, sugar plum, rock sugar, sanding sugar, sugar loaf, super-fine / ultra-fine / bar sugar

ANALYTICAL METHODS ON DIFFERENT FORMULATIONS OF CANE SUGAR

Introduction to Spectrophotometry:

Analytical chemistry is the Science of making qualitative and quantitative measurements. In practice, qualifying an analytic in a complex sample becomes an exercise in problem solving. To be efficient and effective analytical chemist must know the tools which are available to tackle a wide variety of problems. Analytical chemistry deals about analysis of a substance by either qualitatively andquantitatively. A qualitative method provides information about the identity of atomic or molecular species or functional group in a sample.

A quantitative method provides numerical information as to the relative amount of one or more of the components.1, 2. In the past decades, a number of elegant instrumental techniques were reported which are rapid, selective and having a high degree of accuracy. Among these, Spectrophotometry is the most important method, which is widely used for a wide variety of materials. High accuracy, precision, sensitivity and the ease of availability of spectrophotometer made this technique indispensible for the modern Analytical chemists3. Besides, it offers the advantage of having calibration of graphs that are linear over a wide range when compares to other spectroscopic techniques. A very extensive range of concentration of substances (10-2 – 10-8 M) may be covered analytical chemistry plays an important role in the modern especially pharmaceutical and agricultural industries, which rely upon both the qualitative and quantitative chemical analysis while includes UV – VIS, IR, GC and HPLC methods. Titrimetric method is an important and still growing area in the field of analytical chemistry due to its versatility, simplicity and rapidity.

The theory behind spectrophotometric methods lies on a simple relation between the color of the substance and its electronic structure. A molecule exhibits absorption in the UV – Visible region when the radiation causes an electronic transition in molecules containing chromophoric groups. In these techniques color is an important criterion for the identification of constituents.

The importance of Colored solution lies on the fact that the radiation absorbed is the characteristic of the material responsible for the absorption and can be determined quantitatively or qualitatively. Nevertheless a substance that is colorless or faintly colored maybe often determined by the addition of chromogenic reagent, imparting intensive color to the species. The quantitative applicability of the absorption method is based on the fact that the number of photons absorbed is directly proportional

to the number or concentration of atoms, ions or molecules.

ULTRAVIOLET- VISIBLE ABSORPTION SPECTROSCOPY

Spectrophotometry, one of the valuable techniques in pesticide analysis is defined as the method of analysis, which deals with the measurement of spectra. Spectrophotometry is a branch, which embraces the measurement of absorption of radiation energy of definite and narrow wavelength approximating monochromatic radiation by chemical species. This deals with the absorption of electromagnetic radiation in the wave length region 190 to 800 nm. UV absorption spectroscopy deals with absorption of light by a sample in the Ultra Violet region (UV region) is 190 – 380 nm and visible region is 380 – 800 nm.

Absorption spectroscopy (Colorimetry) deals with absorption of light by a sample in the visible region are 380 – 800 nm. Currently research grade UV – Visible absorption instruments come in two configurations. The first is called scanning spectrophotometer because measures the intensity of transmitted light of a narrow band pass and scans the wavelength in order to collect a spectrum. Because absorption is a ratio metric measurement, these instruments generally require the user to measure two spectra, one sample and one blank. The blank should be identical to the sample in every way except that the absorbing species of interest is not present. This can be done either consecutively with a single beam instrument followed by the ratio calculation, or simultaneously with a double beam instrument.

The double beam method is faster, and has added advantage that lamp drift and other slow intensive fluctuations are properly accounted for in the ratio calculation. Collecting spectra with scanning spectrophotometers is slow, but the instruments often have very high resolving power owing to the use of photomultiplier tube detectors, which can be used with very narrow slit widths. Light absorption in the UV-Visible region causes the transition of electrons from ground state to exited state. The important consequences of rapid relaxation of the exited states are not appreciably distributed by absorption of light energy from any source.Therefore, the fraction of light absorbed from an incident beam is independent of the intensity which integrated to obtain Beer's and Lambert's law.

Terms used in absorption spectroscopy

a. Transmittance (T)
   It is the ratio of intensity of transmitted light to that of incident light.
   $T = It / I0$
b. Absorbance (A)
   It is the negative logarithm of transmittance to the base 10.
   $A = - \log 10$
   $T = \log 10\ I0 / It$
   $A = \varepsilon bc$
c. Molar absorptivity (ε)
   When concentration 'c' [$A= \varepsilon bc$] is expressed in mole / lit and cell length in 'cm' then absorptivity is called as Molarabsorptivity.
   $\varepsilon = A / bc$
d. Beer - Lambert's law-
   It can be stated that as the intensity of a beam of monochromatic light when passed through transparent medium decreases exponentially as the thickness and concentration of absorbing media increases arithmetically.
   $A = \log 10\ I0 / It = \varepsilon bc$

Where,
A = Absorbance of the solution at particular wave length of light beam
Io = intensity of incident light beam It = Intensity of transmitted light beam
ε = Absorptivity of molecule at the wavelength of beam
b = Path length of cell in cm
c = Concentration of solution in moles / lit.
Beer's lawis said to be obeyed over a concentrationrange if a plot ofconcentrationagainst absorbance passes through origin and is a straight line.

INDUCTIVELY COUPLES PLASMA – OPTICAL EMISSION SPECTROSCOPY

INTRODUCTION

It has been 25 years since ICP optical emission spectrophotometers (ICP-OES) began to be widely used, and is now one of the most versatile methods of inorganic analysis. Its features are often compared to atomic absorption spectrophotometers. Compared to atomic absorption spectrophotometers, in which the excitation temperature of air-acetylene flame measures 2000 to 3000 K, the excitation temperature of argon ICP is 5000 to 7000 K, which efficiently excites many elements. Also, using inert gas (argon) makes oxides and nitrides harder to be generated.

PRINCIPLE

Inductively coupled plasma, is one method of optical emission spectrometry. When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity.

To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube.

INSTRUMENTATION OF ICP-OES

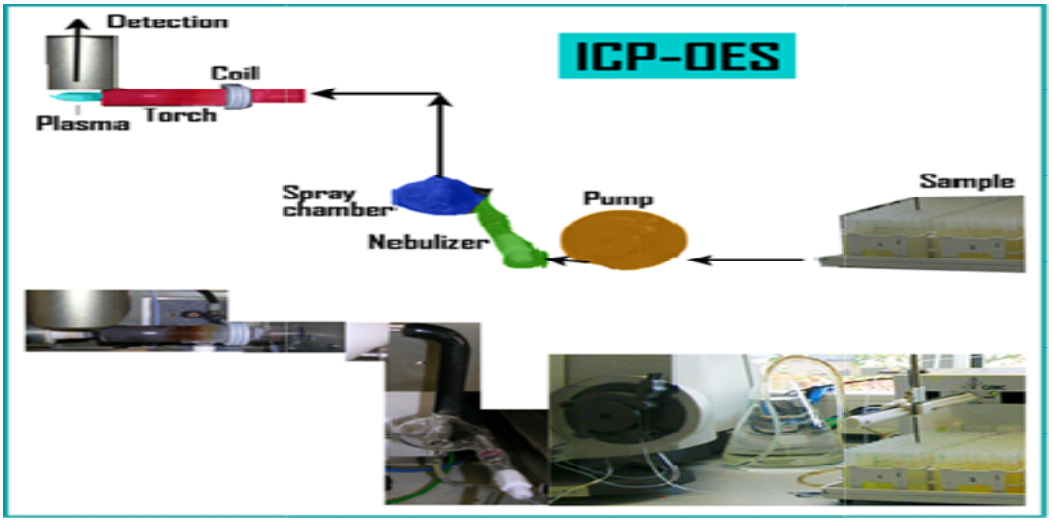

Fig 3 : Schematic Diagram of ICP OES

METHODOLOGY

SAMPLE COLLECTION:

Sugar samples are purchased / collected from the farmers and street vendors in Erode and Coimbatore region as ready for consumption and stored in refrigerator.

SOLUBILITY TEST :

10mg of the sample dissolved in 2ml of solvent.

Polar Solvent :

- ✓ Water
- ✓ Methanol
- ✓ Acetone
- ✓ Acetic acid

Non Polar Solvent:

- ✓ Toluene
- ✓ Chloroform
- ✓ Benzene
- ✓ Pentane

IDENTIFICATION TEST FOR SUGARCANE

1. **Metanil yellow colour:**
   - ✓ Take ¼ part of a teaspoon of the sample in a test tube.
   - ✓ Add 3 ml of alcohol.
   - ✓ Shake the test tube vigorously to mix up the contents.
   - ✓ Pour 10 drops of hydrochloric acid in it.
2. **Chalk powder:**
   - ✓ Dissolve a little amount sample in water in a test tube.
   - ✓ Add few drops of conc. HCL solution.
3. **Sodium bicarbonate:**
   - ✓ Take ¼ of a teaspoon of the sample in a test tube.
   - ✓ Add 3 ml of muriatic acid.
4. **Washing powder :**
   - ✓ Measure ¼ teaspoon of crushed sample into the test tube or glass container
   - ✓ Put on the rubber gloves and measure ½ tsp of muriatic acid or hydrochloric acid into the container.

UV SPECTROSCOPIC METHOD

MATERIALS AND INSTRUMENTS USED

Impurities standard:

Supper phosphate, sodium hydrosulphite and sodium bicarbonate

Chemicals and solvents used :

The selected solvent must give some ideal properties like, the impurities(metals) should be stable in the selected solvent. Hence methanol AR and milli Q water was selected as the solvent for the Impurities(metals). Other solvents used were of analytical grade.

Instruments

- ➢ Shimadzu1800LC-UV spectrophotometer
- ➢ Elico pH meter L1 127
- ➢ Sonica ultrasonic cleaner
- ➢ Shimadzu electronic balance AY 220

UV-VISIBLE SPECTROSCOPIC METHOD

Selection of Solvent:

The UV spectrum of supper phosphate, sodium hydrosulphite and sodium bicarbonate was recorded in various solvents .The spectral pattern and absorbance maxima of supper phosphate, sodium hydrosulphite and sodium bicarbonate were thoroughly analysed. It was found that significant spectra of impurities appeared in methanol and this solvent was selected for determining supper phosphate, sodium hydrosulphite and sodium bicarbonate content in sample by UV spectroscopic method.

Selection of Wavelength:

The stock solution was suitably diluted with methanol, so as to contain 10µg/ml of supper phosphate, sodium hydrosulphite and sodium bicarbonate. This solution was scanned between 800-200 nm in the UV region.

INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROSCOPY

MATERIALS AND INSTRUMENTS USED

Equipment and Apparatus :

- ➢ Microwave Digester or Hot Plate : Multiwave Pro
- ➢ ICP-OES : Shimadzu
- ➢ Balance capable of weighing up to 0.1mg.

Reagents :

- ➢ Suprapure conc. HNO_3
- ➢ HydrogenperoxideMilli Q water
- ➢ Na, Ca,, (NIST traceable standards)

Principle :

A known amount of the sample is digested with conc. Nitric acid in a microwave digester. The digested sample is filtered and diluted to a definite volume and taken for analysis by ICP-OES.

Procedure :

For Metals:

- ✓ Weigh around 0.2 of well homogenized sample into 100 mL beaker.
- ✓ Add 5 ml of Supra pure Nitric acid and 2ml of 30% Hydrogen peroxide and keep with hot plate at 150 °C wait for 15 mins .

- ✓ For every batch take blank, duplicate and spike.
- ✓ After completion of digestion process, let the solutions cool thoroughly.
- ✓ Transfer the solution to a 25 ml volumetric flask and dilute to mark.
- ✓ This is then taken for analysis by ICP OES.

Calibration Range:ICP-OES

Calcium (Ca) : 1, 10, 50 mg/lit
Sodium (Na) : 1, 10, 50 mg/lit

Standard Preparation :

- Initially solution with 500 ppm was taken as stock solution (solution A).
- It was then diluted to 1 ppm by pipetting out 0.2 ml of the above solution (solution A) and make it to 100ml.
- Also converted to 10ppm b diluting of solution A in 10 ml.
- Further, 10 ml of the solution A was diluted to 100 ml to convert to 50 ppm.
- Prepare individual working standards as per the calibration range by diluting a suitable aliquot from working stock **B** and **C** to a volume of 50 ml.
- All dilutions from the Stock solution are made with 5 % of Nitric acid.

Analysis by ICP-OES:

- Switch on the instruments
- Weight till argon purging is completed (approximately 10 mins)
- Tune the instruments with tuning solutions as per the Instruction manual.
- Select the required element(s). Proceed with calibration using Working standards.
- After calibration run the samples. Run blank for every 10 samples.
- Run quality standard for every 10 samples to check instrument performance.

Quantification of metals in sample:

The amount of supper phosphate, sodium hydrosulphite and sodium bicarbonate present in the sample I (jaggery) and sample II (raw sugar) was determined by using slope and intercept values from calibration graph.

Table 4: Preparation and Dilutions

S.no	Elements	Stock solution A (ppm)	Preparation Of sec stock B	Conc. Of sec stock B (ppm)	Preparation Of working stock C	Conc. of working Stock C ppm)	Preparation of working Stock D	Conc of Working Stock D (ppm)
1	Sodium	500	0.2 ml of A solution is diluted to 100 ml	1.0	0.2 ml of A solution is diluted to 10 ml	10	10 ml of A solution is diluted to 100 ml	50
2	Calcium							

RESULTS

SOLUBILITY:

Table 5: Standards

Solvents	Supper phosphate	Sodium hydrosulphite	Sodium bicarbonate
Polar solvents			
Water	Slightly Soluble	Soluble	Soluble
Methanol	Slightly Soluble	Soluble but not clear	Slightly Soluble
Acetone	Insoluble	Soluble	Slightly Soluble
Non polar solvents			
Chloroform	Insoluble	soluble	Insoluble
Toluene	Soluble	insoluble	Insoluble
Benzene	Insoluble	soluble	Soluble

Table 6: Samples

Solvents	Jaggery	Raw sugar	White sugar
Polar solvents			
Water	Soluble	soluble	Soluble
Methanol	Soluble	soluble	Insoluble
Acetone	Soluble but not clear solution	soluble	Insoluble
Non polar solvents			
Chloroform	Insoluble	Completely insoluble	Slightly soluble
Toluene	Insoluble	soluble	Soluble
Benzene	Soluble	Completely insoluble	Soluble

UV SPECTROSCOPIC METHOD

1. **Sodium hydrosulphite**

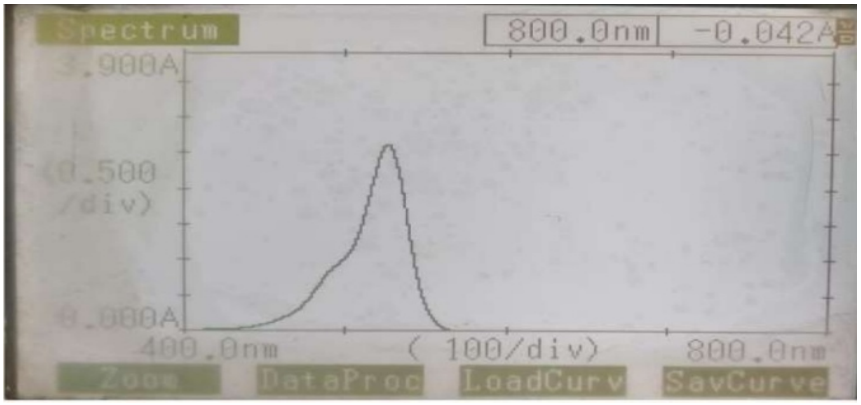

Fig 4: Spectrum of sodium hydrosulphite

The absorbance maxima of sodium hydrosulphite was found to be 520nm

2. **Supper phosphate**

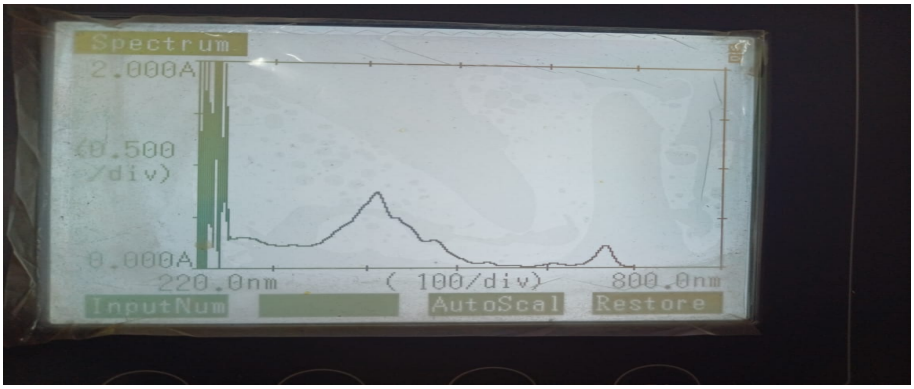

Fig 5: Spectrum of supper phosphate

The absorbance maxima of sodium hydrosulphite was found to be 409nm

3. Sodium bicarbonate

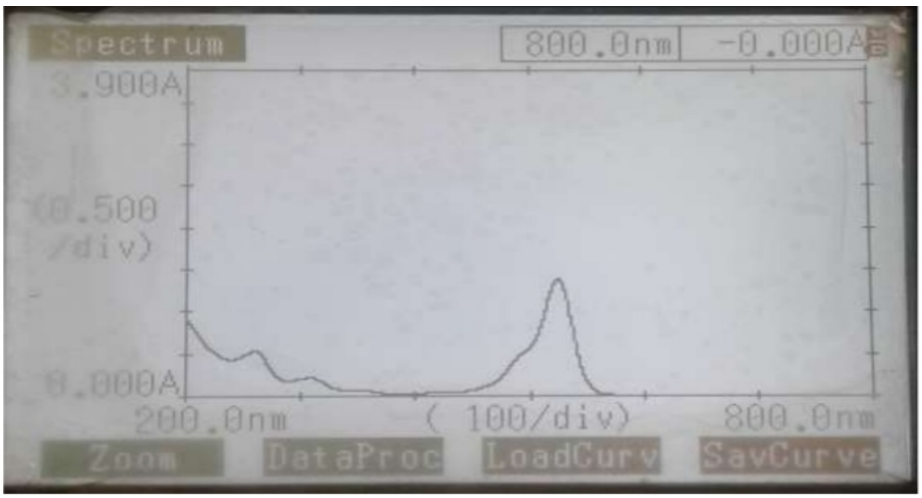

Fig 6: Spectrum of sodium bicarbonate

The absorbance maxima of sodium hydrosulphite was found to be 505nm

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY

A ICP OES method was developed for the quantification of super phosphate, sodium hydrosulphite and sodium bicarbonate in cane sugar products.

QUANTIFICATION OF IMPURITIES PRESENT IN CANE SUGAR BY ICP OES METHOD

Table 7: Optimization of Calcium

Element	Standard	Set. concentration	Intensity
Calcium (Ca)	Blank	0.00	13.987
	Std 1.0	1.0	46.876
	Std 10	10	123.65
	Std 50.0	50	551.624

Table 8: Optimization of Sodium

Element	Standard	Set. concentration	Intensity
Sodium (Na)	Blank	0.00	14.9918
	Std 1.0	1.0	92.3847
	Std 10	10	819.0555
	Std 50.0	50	4527.17

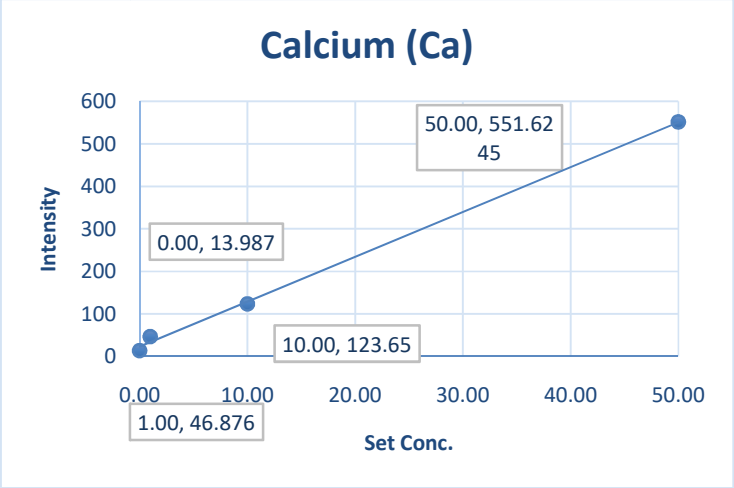

Fig 7: Linearity of Calcium

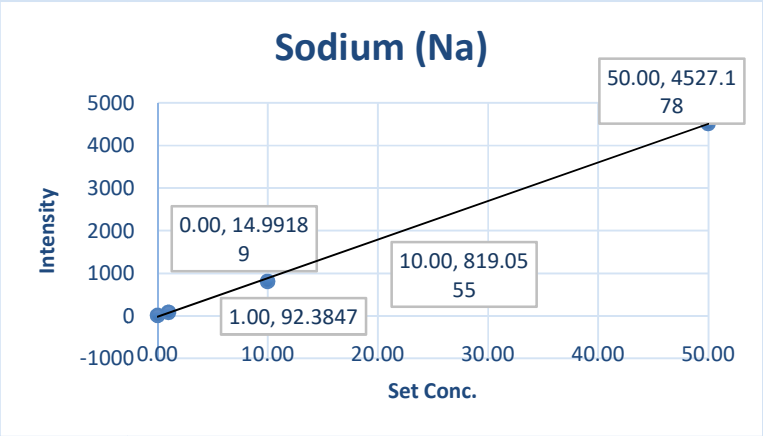

Fig 8: Linearity of Sodium

FORMULA:

$$\frac{[(CONC - BLANK) * DILUTION]}{SAMPLE\ WEIGHT * 10000}$$

Where,
Conc= Sample concentration
Blank = Blank without sample
Dilution = Sample dilution ratio
S. Wt= Sample weight taken for analysis in grams
10000 = Conversion factor (mg / kg to %)

CONVERSION :

= Conc of Elements * molecular weight of required compound / Atomic mass

1. Supper phosphate (calcium dihydrogen phosphate)

$$Ca = \frac{(99.6-18.4)\ X\ 100}{0.2088} / 10000$$
$$= 4.04\%$$

Ca(CaH_2PO_4)2

$= 4.04 \times \frac{234.05}{40.078}$

$= 23.59\ \%$

2. Sodium hydrosulphite (sodium dithionite)

$$Na = \frac{(116-5.52)X\ 100}{0.2020} / 10000$$

$= 5.47\%$

Na $\Rightarrow$ $Na_2S_2O_4$

$= 5.47 \times \frac{174.107}{22.989} = 41.43\%$

3. Sodium bicarbonate (sodium hydrogen carbonate)

$$Na = \frac{(126-5.52)X\ 100}{0.2129} / 10000$$

$= 5.66\ \%$

Na $\Rightarrow$ $NaHCO_3$

$= 5.66 \times \frac{84.007}{22.989}$

$= 20.68\ \%$

SAMPLE – 1

Supper phosphate (calcium dihydrogen phosphate)

$$Ca = \frac{(43.3-18.4)X\ 50}{0.5139} / 10000$$

$= 0.24\%$

Ca($CaH_4PO_4)_2$ $\Rightarrow$

$= 0.24 \times \frac{234.05}{40.078}$

$= 1.4\ \%$

Sodium hydrosulphite (sodium dithionite)

$$Na = \frac{(17.7-5.52)X\ 100}{0.5139} / 10000$$

$= 0.12\%$

Na $\Rightarrow$ $Na_2S_2O_4$

$= 0.12 \times \frac{174.107}{22.989}$

$= 0.91\%$

Sodium bicarbonate (sodium hydrogen carbonate)

$$Na = \frac{(17.7-5.52)X\ 100}{0.5139} / 10000$$

$= 0.12\%$

Na $\Rightarrow$ $NaHCO_3$

$= 0.12 \times \frac{84.007}{22.989} = 0.44\%$

SAMPLE – 2

Supper phosphate (calciumdihydrogen phosphate)

$$Ca = \frac{(32.9-16.4)X\ 100}{0.5012} /10000$$

$= 0.15\%$

Ca $\Rightarrow$ $(CaH_2PO_4)_2$

$= 0.15 \times \frac{234.05}{40.078}$

$= 0.88\%$

Sodium hydrosulphite(sodium dithionite)

$$Na = \frac{(16.3-5.52)X\ 100}{0.5012} / 10000$$

$= 0.11\%$

Na $\Rightarrow$ $Na_2S_2O_4$

$= 0.11 \times \frac{174.107}{22.989}$

$= 0.83\%$

Sodium bicarbonate (sodium hydrogen phosphate)

$$Na = \frac{(16.3-5.52)X\ 100}{0.5012} / 10000$$

$= 0.11\%$

Na $\Rightarrow$ $NaHCO_3$

$= 0.11 \times \frac{84.007}{22.989}$

$= 0.40\ \%$

PERCENTAGE IMPURITIES:

Table 9: Impurities Percentage

ELEMENTS	SUPPER PHOSPHATE	SODIUM HYDROSULPHITE	SODIUM BICARBONATE
Sample – I			
Jaggery	0.24%	0.12%	0.12%
Conversion	0.14%	0.91%	0.44%
Sample – II			
Raw sugar	0.15%	0.11%	0.11%
Conversion	1.88%	0.83%	0.40%

METHOD VALIDATION

- Developed method was validated according to International Conference On Harmonization (ICH) guidelines (Q2R1), Recognized by the FDA for the validation of analytical procedures.
- Analytical method for quantification of raw sugar and jaggery includes accuracy, linearity, range, repeatability, reproducibility, limit of detection and limit of quantification.

1. Linearity :

- ✓ To analyze the linearity of the proposed method with different concentrations of analytes in the range of 1,10,50 (mg/kg) for sodium and calcium.
- ✓ The calibration curves were plotted as intensity Vs concentration of the standard solutions. From the linearity graph the correlation coefficient of calcium and sodium were found to be 0.995 and 0.999 .

Table 10: Linearity range of sodium and calcium

S.no	Concentration (mg/kg)	Sodium	Concentration (mg/kg)	Calcium
1	1	92.3847	1	46.876
2	10	819.0555	10	123.65
3	50	4527.178	50	551.6245

Acceptance Criteria: The results complied with an acceptance criteria since coefficient of correlation was found to be with in the limit i.e.,NLT 0.999.

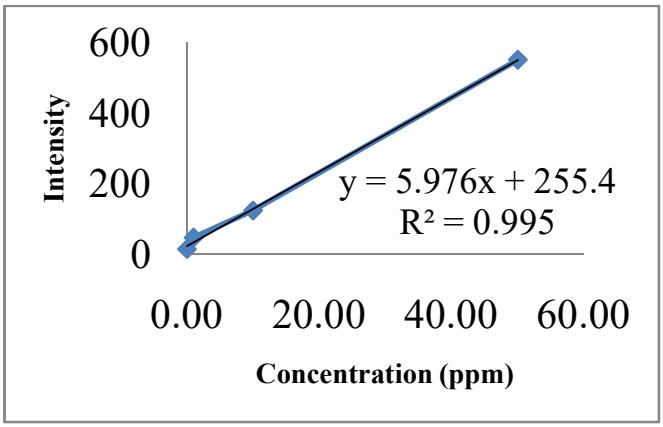

Fig 9: Calibration curve of Sodium

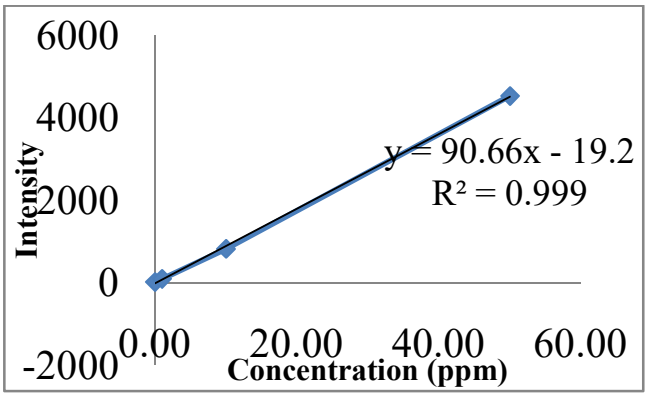

Fig 10: Calibration curve of Calcium

2. Accuracy (% Recovery):

- ✓ The accuracy of the method was determined by recovery studies. A known quantity of the samples was added to pre analyzed same standard at 1,10,50 levels.
- ✓ The recovery studies were carried out 6 times at each level and the percentage
- ✓ Results of accuracy have shown that the mean recovery of the standard is within the specified limit and %RSD is lower than 1.0%.

3. Precision

- ✓ The precision for this method was determined by repeatability and reproducibility.
- ✓ The RSD of the peak area of six replicates was found 1.98 for calcium and 1.6 for sodium in repeatability studies.

recovery for calcium and sodium was found to101.50%,99.58%,101.10% and 99.42%,104.25%,99.23% respectively.

- ✓ Percentage relative standard deviation of the percentage recovery was found to be 0.28% for calcium and 0.31% for sodium.

- ✓ Furthermore, reproducibility studies also performed RSD was found to be 1.82 for calcium and 1.2 for sodium.

4. Limit of Detection and Limit of Quantification

✓ The LOD is the smallest concentration of the analyte that gives a measurable response (signal to noise ratio 3.3). The LOQ is the smallest concentration of the analyte, which gives response that can be accurately quantified (signal to noise ratio of 10).

Table 11: Accuracy (Recovery Studies)

Spike Level	Spike Concentration	Calcium			Sodium		
		Average	% Recovery	% RSD	Average	%Recovery	% RSD
1	1	1.02	101.50%	0.26%	0.99	99.42%	0.41%
10	10	9.96	99.58%	0.38%	10.45	104.25%	0.21%
50	50	50.55	101.10%	0.21%	49.62	99.23%	0.33%

*Each value is the mean of six observations.

Table 12: Repeatability and Reproducibility of the developed method

Elements	Repeatability			Reproducibility		
	Average	SD	%RSD	Average	SD	%RSD
Calcium	0.23	0.04	1.98	0.21	0.03	1.82
Sodium	0.13	0.02	1.62	0.12	0.01	1.21

*Each value is the mean of six observations

Acceptance criteria

The results complied with an acceptance criteria since the percentage relative standard deviation of peak areas of sodium and calcium were found to be with in the limit i.e., NMT 2%.

Table 13: LOD and LOQ

Parameter	Sodium	Calcium
LOD (1ppm)	1.03	1.08
LOQ (10ppm)	10.13	10.01

*mean of five observations

DISCUSSION

- The Purity of Jaggery and Raw sugar is most considerable factor which can cause serious side effects (such as diabetes, Non alcoholicSteathepatitis, mental changes etc..)
- If exceeds the limit.
- From this current study, we had determined the amount of impurities that was added to samples (jaggery and raw sugar) collected from different places.
- The impurities includes Sodium hydrosulphite, Supper phosphate, Sodium bicarbonate (its improve the colour, taste, texture and quantity).
- No such compounds have been detected in High performance thin layer chromatography (HPTLC) because of the absence of fluorescence character.
- Inorganic compounds can be detected using Flame photometry, Atomic absorption spectroscopy, UV-VIS spectroscopy, ICP-OES instrument.
- In this study, the impurities of such elements/metals are detected using ICP-OES.
- Amount of sodium bicarbonate present in jaggery is 4.4g/kg where as the amount of sodium bicarbonate present in Raw sugar is

4.0g/kg, both exceeds the FSSAI limit (325mg-2g /kg)

- As per Australian Food Standards Organization and New Zealand (2014) or FSANZ has set the standard for sodium hydrosulphite in food (Maximum permitted level) not more than 1g/kg. From the study, amount of sodium hydrosulphite present in jaggery is 9.1g/kg and sodium hydrosulphite present in Raw sugar is 8.3g/kg, hence it exceeds the limit.
- Amount of supper phosphate present in jaggery is 14g/kg and amount of supper phosphate present in Raw sugar is 18.8g/kg, both exceeds the FSSAI limit (100 to 350 mg /kg).

SUMMARY AND CONCLUSION

- The percentage impurities of inorganic compounds (elements/metals) like sodium and calcium are identified using an instrument ICP-OES.
- Manufacturing of jaggery and raw sugar in small scale industries must contain soda lime and coconut oil which is a pure form of jaggery and raw sugar.
- From the samples collected and tested, it results in the usage of elements/metals like sodium bicarbonate, sodium hydrosulphiteand supper phosphate for the improvisation of texture, quantity.
- From the result, we conclude that all the elements/ metals like sodium bicarbonate, sodium hydrosulphite and supper phosphate exceeds the limit.
- The developed method was validated for various parameters like Accuracy, precision, Linearity, limit of detection and limit of quantification and was found to be satisfactory.

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