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AN ASSESSMENT OF PHOSPHATE AND SULPHATE CONTENTS IN RAW AND PROCESSED SUGARS

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Abstract
Sugar (raw and processed) is consumed in considerable amount in Pakistan annually. In this study, thirteen locally marketed raw and processed sugar brands have been analyzed for phosphate and sulphate contents. Analyses have been carried out using spectrophotometric methods. Results show that phosphate contents were found to be in the range of 1710-3315 $\mu g\ g^{-1}$ and 0.4 – 216 $\mu g\ g^{-1}$ in raw and processed sugar samples respectively. Sulphate contents were found in the range of 34.11– 62.01 mg g^{-1} and 36.19–111.80 mg g^{-1} in raw and processed sugar samples respectively. In general, phosphate contents were observed to be comparatively higher in raw sugars, whereas sulphate contents were comparatively higher in processed sugars. This study provides baseline data on phosphate and sulphate contents in locally marketed raw and processed sugars.

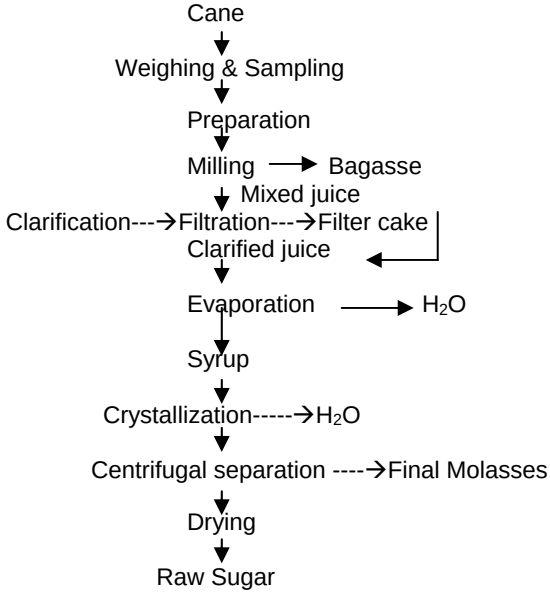
Keywords: Assessment, phosphate, raw and processed sugars, sulphate.

INTRODUCTION
Sugar term is applied loosely to any of a number of chemical compounds in carbohydrate group that are readily soluble in water, colorless, odorless, usually crystallizable and more or less sweet in taste. In general all monosaccharides, di-saccharides and tri-saccharides are termed as sugars and distinct from polysaccharides such as starch, cellulose and glycogen. Sugars, widely distributed in nature, are manufactured by plants during the process of photosynthesis and are found in animal tissues. Electron microscope image of raw cane sugar reveals the shape of sugar crystals (Fig.1).
Sucrose is present in limited quantities in many plants, including various palms and the sugar maple, but the sugar beet and the sugarcane are the only commercially important sources. More than half of the world's sugar supply is obtained from the sugarcane, which is grown in tropical and subtropical climates. The rest is supplied by the sugar beet, which is grown in temperate countries. Sugar beets are the chief source of sugar for most of Europe and are grown extensively in Russia, Ukraine, Germany, France, and Poland. The northwestern U.S. is also a center of sugar beet production; sugarcane is grown in the U.S. in

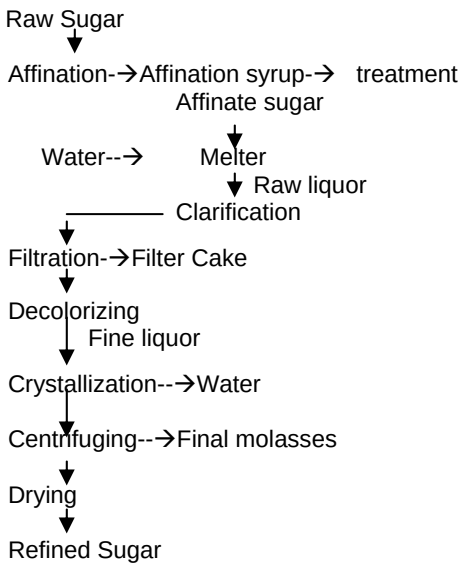
Hawaii, Louisiana, and Florida; it is also grown in Puerto Rico. The countries producing the largest amounts of sugar include Brazil, Cuba, Kazakhstan, Mexico, India, and Australia. Demand of sugar in Pakistan has been estimated to be more than 2.5 million tons [Zafar 1993].

Fig. 1: Sugar Crystals

Sugar Factory doesn't really manufacture sugar. The sucrose is synthesized by processes of nature in the cane plant, so called manufacturing process is essentially one of separating the sucrose from various materials with which it is associated in the cane plant. Juice is separated from the fiber insoluble portion of cane. Clarification removes suspended, colloidal and soluble materials. Evaporation removes water from the juice. Raw sugar contains 98-99% Sucrose [Glaszion *et al.* 1962]. It is then refined; Steps involved in refining process include Affination, Clarification, Decolorizing, Crystallization, Drying and Finishing [Meade 1963] as shown in the flow charts below:



Flow sheet for the sugar manufacturing process.



Flow Sheet for the Sugar Refining Process

Abram and Ramage [1979] have reported ash contents i.e. 0.45% and 0.007% in raw and refined sugars respectively at Thames Refinery, London, United Kingdom. But no specific data has been reported on levels of phosphate and sulphate in raw and refined sugars. Similarly no report has been found on phosphate and sulphate contents of raw and processed sugars marketed in different cities of Pakistan. This study aims to assess phosphate and sulphate contents of locally marketed raw and processed sugars.

Table 1: Composition of Raw and Refined Sugars [Abram and Ramage 1979]

Components	Raw Sugar	Refined Sugar
Sucrose	97.73 %	99.95 %
Invert	0.56 %	0.006 %
Ash	0.45 %	0.007 %
Organic Content	0.62 %	0.014 %
Moisture	0.64 %	0.023 %

MATERIALS AND METHODS

CHEMICALS

Analytical Reagent Grade chemicals i.e. $K(SbO)C_4H_4O_6.0.5H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$, $C_6H_8O_6$, H_2SO_4, $SnCl_2.2H_2O$, $(NH_4)_2SO_4$, HCl supplied by Merck were used without further purification. Deionized water was used throughout this research work.

GLASSWARE AND EQUIPMENT

Officially calibrated Pyrex glassware was used throughout. Instrument used were UV/Visible Spectrophotometer (Cecil), Electrical balance (AW220, Shimadzu, Japan) etc.

SAMPLE COLLECTION

Thirteen sugar (raw and processed) samples of different brands were collected from local market of Multan city. Precautions were followed to avoid any sort of contamination of the samples. All glassware used was carefully cleaned following standard procedures. Details of sugar samples and their manufacturer are given in the Table 2.

Table 2: Sugar Samples and their Manufacturers.

Sample No.	Sample type	Manufacturer
1	Sugar	Ansari Sugar Mills , Karachi
2	Sugar	Kohinoor Sugar Mills, Khushab
3	Sugar	Dewan Sugar Mills, Sindh
4	Sugar	Punjab Sugar Mills, Punjab
5	Sugar	Fatima Sugar Mills, Muzaffargarh,Punjab
6	Sugar	Sanger Sugar Mills,Sindh
7	Sugar	Ghotki Sugar Mills,Ghotki ,Sindh
8	Sugar	Sheikhu Pura Sugar Mills, Sanawan, Muzaffargarh
9	Sugar	Hamza Sugar Mills, Khan Pur
10	Icing Sugar	Rossmoor Food Products, Karachi
11	Shakkar (unbranded)	Provenance unknown
12	Black Gur (unbranded)	Provenance unknown
13	White Gur (unbranded)	Provenance unknown

DETERMINATION OF PHOSPHATE

Preparation of Standard Solutions

- 1000mg L^{-1} Phosphate standard stock solution
  0.4716g K_2HPO_4 was dissolved in deionized water and final volume was made up to 100$cm^{3.}$
- 100.0 mg L^{-1} Phosphate Standard solution
  10.0 cm^3 of 1000ppm PO_4^{3-} stock solution was diluted up to 100cm^3.
- 10.0 mg L^{-1} Phosphate Standard solution
  10.0 cm^3 of 100 ppm PO_4^{3-} stock solution was diluted up to 100cm^3

Working Standards

Concentrations of working standards were 0.5, 1.0, 1.5, 2.0, 2.5 mg L^{-1} by taking 2.5, 5.0, 7.5, 10.0, 12.5 cm^3 of 10.0 mg L^{-1} phosphate standard respectively and finally diluted to 50.0 cm^3 with water after addition of reagents.

Reagents

Potassium Antimony Tartarate Solution ($K(SbO)C_4H_4O_6.0.5H_2O$):
0.27g K $(SbO)C_4H_4O_6.0.5H_2O$ in deionized water and the final volume was made 100mL.

Ammonium molybdate solution ($(NH_4)_6MoO_{24}.4H_2O$):
4.0 g in 100mL water.

Ascorbic Acid Solution:
1.76g was dissolved in deionized water and the final volume was made 100mL. If stored at 4°C it can be used for one week.

Concentrated Sulfuric acid:
7.0mL in 50mL water.

Preparation of Reaction Mixture

10.0 mL H_2SO_4+ 1.0 mL $K(SbO)C_4H_4O_6.0.5H_2O$ + 3.0 mL $(NH_4)_6MoO_{24}.4H_2O$ + 6.0 mL Ascorbic Acid solution into 25mL measuring flask and mixed well, then cooled to room temperature (25°C). A clear solution was obtained which was stable for 240 minutes.

Determination of Phosphate in standards and sugar samples

Spectrophotometric procedure [Radojevic and Bashkin 1999] was followed to determine Phosphate contents in standards and sugar samples:

Standards

To aqueous solutions containing phosphate contents equivalent to 0.1-2.5 ppm in 50 ml measuring flask, 10 ml of deionized water and 8.0 mL of the reaction mixture were added. Volume was made up to the mark with deionized water. Absorbance of each solution was measured at 880 nm against reagent blank.

Samples

To 2.5 g of sugar sample in 50 ml measuring flask, 10 ml of deionized water was added, and mixed well to dissolve sugar contents. Then 8.0 mL of the reaction mixture was added. Volume was made up to the mark with deionized water. Absorbance of sample solution was measured at 880 nm against sample blank.

DETERMINATION OF SULPHATE

Preparation of Standard Solutions

- 1000mg L^{-1} Sulphates standard solution
  1.375g $(NH_4)_2SO_4$ was dissolved in deionized water and final volume was made up to 100cm^3**.**
- 100.0 mg L^{-1} Sulphates Standard solution
  10.0 cm^3 of 1000 ppm SO_4^{2-} stock solution was diluted up to 100 cm^3.
- 10.0 mg L^{-1} Sulphates Standard solution
  10.0 cm^3 100 ppm SO_4^{2-} stock solution was diluted up to 100 cm^3

Working Standards

1.0, 2.0, 3.0, 4.0, 5.0 mg L^{-1} were prepared by taking 5.0, 10.0, 15.0, 20.0, 25.0 cm^3 of 10.0 mg L^{-1} Sulphate standard respectively and finally made up to 50.0 cm^3 with water after addition of reagents.

Reagents

- $M(NH_4)_6Mo_7O_{24}.4H_2O$
  1.766g $(NH_4)_6Mo_7O_{24}.4H_2O$ in deionized water and the final volume was made 100mL.
- 0.1M $SnCl_2.2H_2O$
  2.25g $SnCl_2.2H_2O$in deionized water and made the final volume 100mL.
- 11.6 M HCl (36-37%)

Chemical Reduction of Mo (VI) to Mo (V)

50.0mL (0.1M) Mo (VI) solution +21mL HCl (11.6 M) + 25mL $SnCl_2.2H_2O$ (0.1M) with constant stirring(Resultant: Orange Red Solution).The final volume was

made up to 100mL with deionized water and stored in dark at 10°C.When required Mo(VI) and Mo(V) were used in 1.5:1 v/v ratio.

Determination of Sulphate in standards and sugar samples

Spectrophotometric procedure [Niazi *et al.* 1991] was followed to determine sulphate contents in standards and sugar samples.

Standards

In a 50 ml round bottom flask fitted with a reflux condenser, containing sulphate ion solution (equivalent to 0.25-1.25 ppm), 3ml of reagent mixture consisting of Mo(VI): Mo(V) (1.5:1) mole ratio in 4 M HCl, 6.5ml of 4 M HCl and 1.5ml of water were added. Volume was made up to 25 ml by addition of 12.5 ml of acetone, so that final solution should contain acetone 50% V/V. After thorough mixing, the solution was refluxed at 82°C in a water bath for 1hour. After cooling to room temperature in about 20 minutes, Absorbance of each solution was measured at 725nm against reagent blank.

Samples

Sugar sample (0.0222 - 0.0274 g) was taken in a 50 ml round bottom flask fitted with a reflux condenser; 3 ml of deionized water was added. The mixture was stirred to dissolve sugar contents. 3ml of reagent mixture consisting of Mo(VI): Mo(V) (1.5:1) mole ratio in 4 M HCl, 6.5ml of 4 M HCl were added. Volume was made up to 25 ml by addition of 12.5 ml of acetone so that final solution should contain acetone 50% V/V. After thorough mixing, the solution was refluxed at 82°C in a water bath for 1hour. After cooling to room temperature in about 20 minutes, Absorbance of each solution was measured at 725 nm against sample blank.

RESULTS AND DISCUSSION

In this work, thirteen locally marketed raw and processed sugar samples have been assessed for phosphate and sulphate contents using reported UV-Visible spectrophotometric methods. Estimated phosphate and sulphate contents in raw and processed sugar samples are given in the Tables 3 and 4. Calculated daily intake of phosphate and sulphate based on the results presented in Tables 3 and 4 are given in Table 5.

Table 3: Phosphate Levels Estimated in Raw and Processed Sugar Samples.

Sample No.	Mean* Phosphate Contents ($\mu g.g^{-1}$)	Standard Deviation	Relative Standard Deviation (%)	Range (min.-max.)
1	15.6	0.4	2.4	(49.67 - 50.15)
2	22.7	0.8	3.7	(21.9 - 23.5)
3	14.1	0.9	6.6	(13.2 -15.1)
4	14.7	0.2	1.3	(14.5 -14.7)
5	25.0	0.8	3.2	(24.1 -25.6)
6	32.3	0.3	0.9	(32.0 -32.6)
7	41.3	0.2	0.5	(41.2 -41.6)
8	0.4	0.5	117.1	(0.0 -0.9)
9	1.6	0.3	17.0	(1.4 -1.9)
10	216	15	0.5	(201-231)
11	3315	15	0.6	(3300-3330)
12	1710	10	10	(1700-1720)
13	1972	192	6.9	(1750-2095)

* Mean of triplicate determinations

Table 4: Sulphate Levels Estimated in Raw and Processed Sugar Samples.

Sample No.	Mean* Sulphate Contents (mg g^{-1})	Standard Deviation	Relative Standard Deviation (%)	Range (min.-max.)
1	73.06	3.11	4.3	(70.33 - 76.44)
2	49.87	0.25	0.5	(49.67 - 50.15)
3	80.44	0.22	0.3	(80.27 -80.69)
4	111.80	0.51	0.5	(111.34 - 112.35)
5	72.97	6.72	9.2	(65.29 - 77.77)
6	75.19	3.67	4.9	(72.46 - 79.36)
7	62.44	0.59	0.9	(62.05 - 63.11)
8	71.91	0.66	0.9	(71.18 - 72.46)
9	78.07	0.78	1.0	(77.19 - 78.67)
10	36.19	0.41	1.1	(35.72 - 36.50)
11	62.01	0.29	0.5	(61.70 - 62.28)
12	59.19	0.51	0.9	(58.69 - 59.70)
13	34.11	0.81	2.4	(33.23 - 34.82)

* Mean of triplicate determinations

Table 5: Calculated Daily Intake of Phosphate and Sulphate from Raw and Processed Sugar Samples.

Sample No.	Phosphate Intake (μg)			Sulphate Intake (mg)		
Daily Sugar Intake	1g	5g	10g	1g	5g	10g
1	15.4	77	154	73.06	365.3	730
2	22.7	113.5	227	49.87	249.35	499
3	14.1	70.5	141	80.44	402.2	804
4	14.7	73.5	147	111.8	559	1118
5	25	125	250	72.97	364.85	730
6	32.3	161.5	323	75.19	375.95	752
7	41.3	206.5	413	62.44	312.2	624
8	0.4	2	4	71.91	359.55	719
9	1.6	8	16	78.07	390.35	781
10	216	1080	2160	36.19	180.95	362
11	3315	16575	33150	62.01	310.05	620
12	1972	9860	19720	59.19	295.95	592
13	1710	8550	17100	34.11	170.55	341

Results show that phosphate contents were found to be in the ranges 1710 - 3315 μg g^{-1} and 0.4 – 216 μg g^{-1} in raw and processed sugar samples respectively, whereas sulphate contents were found in the ranges 34.11 – 62.01 mg g^{-1} and 36.19 – 111.80 mg g^{-1} in raw and processed sugar samples respectively. In general, phosphate contents were found to be comparatively higher in raw sugar samples and sulphate contents were comparatively higher in processed sugar samples. Probable source of higher phosphate contents in the sugar samples may be the bone char which is used to remove color by most of the refineries. Bone char is prepared by heating bones in the absence of air followed by grinding to a suitable granular condition. Bone char contains carbon in a very active form on a porous base of calcium phosphate (Ca_3PO_4). Phosphates should be removed as completely as possible in clarification process. Soluble phosphate content greater than 8-10 ppm indicates insufficient precipitation. Higher sulphate contents may be attributed to the sulphitation process used by some cane sugar mills to produce white sugar. In the sulphitation process, the expressed juice from the mills is heated to 75°C, clarified with lime and sulfur dioxide and in some cases filtered and then evaporated. After the syrup is treated with sulfur dioxide again, it goes through a

three- or four –boiling system. Sugars are mixed with high purity syrup and centrifuged, dried, screened for size and distributed as white sugar [Kent 1974].
This study provides baseline data on phosphate and sulphate contents in locally marketed raw and processed sugars. The data may prove useful in correlating phosphate and sulphate levels in sugars and *diabetes mellitus* which is a subject of further research in our laboratory.

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