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STUDY OF HEAVY METAL CONTENT IN THE REGIONAL FRUITS USING SPECTROPHOTOMETER[#]

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Abstract

Vegetables have become an integral part of human's diet due to their nutritional values thus any form of contamination especially by heavy metals is of great concern. As Konkan Region is rich in nature, due to the soil present in this area there are several fruits, vegetables and the plants are present with the biodiversity, though the soil also contains many minerals and the presence of or are observed in this area. But day-to-day, the increase in the use of agricultural lands for mining due to this most of the agricultural lands are nearby areas of mining. Fruit and vegetables are rich sources of vitamins, minerals, and fibers and also have beneficial antioxidative effects. However, the intake of heavy metal-contaminated fruit and vegetables may have a risk to human health; hence the heavy metal contamination of foods are one of the most important aspects of food quality assurance. Therefore, to investigate the contamination of heavy metals in the fruits we have taken four major fruits which are widely available in this region. i.e. *Musa velutina* (banana), *Cucumis sativus* (Kakadi), *Ananas comosus* (Pineapple), *Cucumis melon* (Muskmelon) for the determination of Pb, Cd, Zn, Cu, Ni, Fe and Cr metals. As the above fruits are widely found in Konkan region and they bear very much quantity of water, so we decided to take these fruits for the study which have very much impact of the metal or minerals available in the soil or water. Those minerals and metals are present in very minute quantity so we have used spectrophotometer for the determination of such small quantity. There is growing awareness about the efficacy of essential elements in the maintenance of good health and prevention of diseases. Zinc plays a vital role in wound healing, immune system, reproductive system and nervous system. Zinc wades off oxygen free radicals and also a din metabolism of carbohydrates by assisting insulin into function. Chromium lowers blood sugar and also works with insulin in metabolization of sugar, while copper is required for conversion of body's Fe into hemoglobin. Copper lowers low density lipoprotein (LDL) *cholesterol*, raises high density lipoprotein (HDL) *cholesterol* and prevent oxidation of low-density lipoprotein (LDL) *cholesterol*. Iron is necessary for production of haemoglobin, immune functioning and drug detoxification. Manganese aids in

maintenance of blood glucose level, synthesis of interferon, energy production and bone growth. In this study Pb, Cd, Zn, Cu, Ni, Fe and Cr in selected traditional fruits growing/found in Konkan region were determine during spectroscopy.

Keywords: Fruits, Heavy metals, spectroscopy, konkan

#Research Article

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Introduction

A metal of relatively high density (Specific gravity greater than about 5) or high relative atomic weight is defined as a Heavy metal. The term heavy metal is used to describe more than a dozen elements that are metals or metalloids e.g. Cd, As, Cr, Pb, Hg, Mn etc. heavy metals are naturally constituents of the earth's crust, because they cannot be degraded or destroyed, heavy metals are persistent in all parts of the environments therefore, heavy metals can be described as any metallic element that has a relatively high density and is toxic or poisonous at low concentration.

Human activities affect the natural geological and biological distribution of heavy metals through pollution of air, water and soil. Human are also responsible for altering the chemical forms of heavy metals released to the environment.

Some heavy metals such as Hg and Pb are toxic metal that have no knownvital or beneficial effect on organism and accumulation over time in the bodies of animal can cause serious illness. In small quantities certain heavy metals are nutritionally essential for a healthy life. (e.g. Fe, Cu, Mn, and Zn). Some of these are referred to as the trace elements. These elements and some form of them are commonly found naturally in food stuffs, in fruits and vegetables, and in commercially available multivitamin products. Much research has been conducted on heavy metal contamination in soil from various anthropogenic source such as industrial waste, automobile emission and agricultural practices.

Bioavailability is defined as the fraction of the elements from an ingested matrix such as soil, water or food that can be absorbed by an organism. *Jaradat and Momani* have been reported in 1998 that the bioavailability and environmental mobility of metals are dependent upon the form in which the metal is associated with the soil. Soon and Bates in 1982 have been reported metal distribution among specific forms varies based on the metal's chemical properties and soilcharacteristic. Thus it is important to evaluate the availability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of heavy metal contaminants in soil.

Bernhard et al, 1986 have been reported the distribution of trace elements in the environment, their accumulation by organism, their bio availability and their toxicity to organisms (including humans) can be understood only in terms of trace element species. Soil consist of heterogeneous mixture of organic and inorganic solid component as well as a variety of soluble substances. Since the behavior of theelements in a soil-water-plant

system depends on their chemical forms, single or sequential extraction is most useful in separating the different bound states. The procedure involve subject in gasolid sample (soil or sediment) to successive extraction with reagent possessing different chemical property (acidity, redox potential or complexing behavior) in which each extract includes a part of the trace metals associated with the sample.

Experimental results are obtained by using spectrophotometer. In these experiments used fruits are widely found in Konkan region and they bear very much quantity of water, some decided to take this fruits for the study which have very much impact of the metal or mineral available in the soil or water. Those minerals and metals are present in very minute quantity so we have been used spectrophotometer for the determination of such small quantity.

Plants have inherent capacity to uptake toxic substances including heavy metals and radionuclides which may subsequently get transferred along the food chain (Rattan *et al.*, 2005). Higher concentrations of heavy metals and radio nuclides in plant tissues may cause toxicity to human being or other living species feeding on them (Alloway and Ayres, 1997). The contaminants transfer from Agricultural soil to plant is the major pathway of human exposure to them as the soil is an important resource that is used for food production (Rattan *et al.*, 2005). Accumulation of heavy metals in soils, their uptake by crop plants followed by their subsequent movement in food chain is of great concern.

The Mining industry in India is a major economic activity which contributes significantly to the economy of India. Western Ghat area of Maharashtra, also known as the Konkan coast, is a rugged section of the western coastline of India. In Konkan region there is huge amount of biodiversity is present, in this region there are many types forests and different types of Vegetation are found Konkan region is a naturally gifted with various rare biodiversity. Konkan is well known for its natural beauty as well as tourism and its greenery, with clean beaches. As the point of natural sources, the soil is also one of the significant natural resource, which contains various ores of most heavy metals such Fe, Mn, Cu, Al along with Au (gold). The soil of south konkan is mainly of alluvial and residual types as well as Lateritic soil are found in this area.

In Konkan region, there are so many fruits are cultivated such as Banana, Cucumber, Pineapple, Muskmelon, Chikoo, Mango, Cashew *etc.* In the cultivation of such fruits this soil, the plants also absorb water, essential nutrients; minerals along with the heavy metals present in the soil through root system. Asaniye is a small village on the Konkan coast in Maharashtra, surrounded by thick forests of the Western Ghats. In this area mining of Mn, Iron or Fe are found. One of the firms operating in Redi, denied mining was causing health problems. Mining involves various activities for extraction of minerals and metals from the earth. The heavy metal content of these samples obtained from mine site to study the distribution pattern of trace metal due to mining activity.

Results indicated that the soil samples have very high content of heavy metals, like iron being determined in the range of 2092-3106 mg kg⁻¹ and highest concentration of it was 5284 mg kg⁻¹ in blended hematite quartz soil sample. However, the concentrations of trace metals in water sample were still within the permissible limits according to the drinking water quality standard of WHO. This heavy metal is present in soil due to mining and plants are absorbed some heavy metals and minerals from soil. So plants and fruits in nearest mining area contain harmful heavy metal content.

Iron ore mines acts as an important source of major metals, mainly Fe and Mn and also contributes for trace metal into the environments. Mining and metal processing activities led to distribution of metals in surface environment.

In India, there are many types of fruits are cultivated and exported in many countries. These fruits are used for many purposes and some fruits which also contains water, minerals, vitamin, protein but these contains in minute amount of heavy metals which are very harmful for the human body.

There are many methods to determine or estimate the concentration of heavy metal in ppm level in fruit juice. There is a specific area which contains more amount of cultivation of specific types of fruits. In the local region, many varieties of fruits are found in specific seasons likewise in rainy season particularly in Konkan region there are Banana, Pineapple, Coconuts etc. fruits are occurred. In winter season, there are Papaya Gava fruits are available. In summer season Mango, Watermelon, Muskmelon, Cucumber etc. high-water content fruits are available.

We all know fruits are grow in soil. Soil is thin covering on the land which supports the growth of plants. It is significant factor in determining the nature and type of vegetation. It helps in providing water and minerals to the land and plants. The soil in this region as well as soil which is near seashore or near river, also contain high amount of heavy metals.

These heavy metals are very harmful for human being or other animals. The human consumes fruits or fruits juice which contains heavy metals are directly effects on their digestive, reproductive or respiratory system. Some heavy metals are harmful for small children, pregnant women or those which have weak immune system. The heavy metals are such as Hg, As, Cr, Cu, Fe, Ni, Zn, Pb etc. are toxic metals. The arsenic is generated from fossil fuel burning fertilizer plants

Liquid effluents contain elemental arsenic ranging from 0.27 to 3.2 mg/L. Arsenic is present in soil as well as fruit mostly in industrial area.

In Konkan region chromium, copper, cadmium, iron, lead, zinc, nickel these heavy metals are generally occurs in the soil. The toxicity of Cr to aquatic life which also enters in the mammalian body i.e respiratory, digestive and dermal system which shows that only 6% or less Cr compound were absorbed. The abundance of Cd in the earth crust with an average concentration of 0.2 ppm. The acute toxicity symptoms of Cd poisoning are abdominal pain associated with Nausea, Vomiting, Diarrhea, Headache and Kidney damage. It also caused generalized cancers in laboratory animals and has been linked epidemiologically with certain human cancers. The permissible limits of Cd in drinking water is 0.05 mg/L.

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. 1, 2-Dihydroanthraquinone-3-sulphonic acid, Sodium salt (*Alizarin Red-S*) has been reported as spectrophotometric agents for Arsenic.

Lead is in trace amount is important industrially as a toxicant; biological nutrient, environmental pollution and occupational hazard. Lead is a serious cumulative body poison. Organic lead compounds such as Tetramethyl lead are highly poisonous because they are absorbed readily by the body through skin and mucus membrane. 1, 5-Diphenylthiocarbazone (Dithiozone) is one of the most widely used photometric reagent and forms colored water insoluble complex with large number of metal ion. The aim of the

present study is to develop a simpler direct Spectrophotometer method for the trace determination of lead in human fluid with dithizone in the presence of inexpensive cationic micelles such as cetyltrimethyl ammonium bromide (CTAB) in aqueous solution. Acute lead poisoning in human causes severe damage in kidney, liver, brain, reproductive system and sometime causes death.

Zinc is the 2nd most abundant transition element in human body. Zinc is found in rice, cereals, meat, liver, oysters and nuts in several enzymes and DNA binding proteins. It has a significant physiological role in human being in mammalian reproduction, gene transcription function, brain function and pathology. The symptoms of Zn deficiency lead to loss or decrease of fertility, sickle cell disease, high level of Zn cause Wilson's disease etc. The determination of Zn at micro levels by several techniques such as Spectrophotometry, AAS, polarography, ICP-AES, Voltammetry and other technique. However, the methods are having stage like less selectivity and sensitivity, time are given. So there is great need to develop efficient and eco-friendly method for the determination of Zn (II).

Nickel A transition element, commonly exists in +2 oxidation state though +1, +3 and +4 states are also observed in complexes of nickel. It is used in many industrial and consumer products like stainless steel, nickel brass, catalyst etc. Nickel plays an important role in biological system as constituent of several enzymes. It is also present in soil and plants. The conc. of nickel in these applications varies widely, from trace quantities to being a major constituent. Di-methyl glyoxime (DMG) forms a red colored complex when treated with an alkaline solution of nickel in presence of an oxidizing agent such as bromine. The red complex of Ni-DMG contains nickel in higher oxidation state. The complex absorbs at about 445 nm.

Estimation of copper in solution and in a number of alloys and metals, as also in semi-conductors has been the subject of recent interest. For this purpose series of reagents like Dithizone, Thiobenzamide, 2-Methyl-8-quinolinol, Nitrotriacetic acid, Diethyl dithio carbamate, Ethylene diamine tetra acetic acid etc. have been developed for colorimetric estimation of copper.

It is known that **EDTA** forms a soluble complex with copper using this properly, simple methods for estimation of copper in steel, bronze and other alloys have been developed. Malmstadt and Gohrb and recorded the absorption of copper nitrate versant and copper versant solution in the ultraviolet region and used the absorption at 320nm for estimation of copper with versant and vice versa. This method appeared useful on account of the possibility of using the characteristic absorption of copper in the visible region. (at 630 μ)

Materials and Methods

Preparation of stock solution of fruit juices: (General Method)

Take fruit and grind them in a mixer. After that take all the extraction beaker, add about 10-15 cm³ absolute alcohol, boil the solution in water bath for half an hour the solid separated and alcohol is evaporated, Filter the solution using cotton plug, boil the solutions Concentrate the solution add 10 ml of 2N Acetic acid in 100 cm³ flask as a preservative and dilute the flask up to the mark with distilled water. This is stock solution.

Result and Discussion

All the fruit samples are prepared and analyzed as per the said procedure and the n all the obtained results are calculated through least square method which are summarized as - From the obtained results, Banana fruit (*Musa velutinas*) have very much amount of heavy metals like Cr, Fe, Pb, Zn, Cu, but Cd and Ni are less amount than other three fruit juice which is Cucumber (*Cucumis sativus*), Pineapple (*Ananas pineapple*) Muskmelon(*Cucumismelon*).

In Cucumber Fruit (*Cucumis sativus*) contain only Pb is in high amount while other heavy metals like Cr, Fe, Zn, Cu, are in less amount. But Ni is very less quantity obtained. In Ananas fruit (*Ananascomosus*), Fe, Zn and Pb have very much amount isobtained.whileother metalslike Cr, Cd, Cu, Ni are in less quantity. The Muskmelon fruit contain Fe, Pb, Zn, Cu is in high amount. Whereas Cr, Cd are in less amount is obtained, but Ni is obtained in very less amount.

All the obtain results are summarized here as:

Fruit	Cr		Fe		Pb		Cd		Zn		Cu		Ni	
	nm	ppm	nm	ppm	nm	ppm	nm	ppm	nm	ppm	nm	ppm	n m	pp m
Banana	0.658	6.11	0.122	13.26	0.488	24.4	0.697	4.05	1.473	43.32	0.083	5.92	0.453	2.07
Cucumber	0.065	0.6	0.012	1.27	0.134	6.7	0.275	1.59	0.079	2.32	0.033	2.34	0.189	0.86
Pineapple	0.123	1.13	0.109	11.9	0.063	3.5	0.242	1.40	0.578	17.00	0.032	2.28	0.297	1.36
Muskmelon	0.512	4.76	0.125	12.71	0.318	15.9	0.496	2.88	0.248	7.29	0.088	6.28	0.391	1.79

Comparison between Permissible Limit and Result Obtained

Hence, from the discussion, we see that the Banana fruit have very much amount of Zn, Pb than the other fruits; where as the smallest amount of Nickel is present in all fruits.

Whereas, all the fruit juice contains much more quantity of heavy metals above the permissible limit of WHO. According to this we conclude that:

The permissible limit of Cr is 0.05ppm. all fruits are above the permissible limit of Cr. i.e. Banana fruit contain 6.11 ppm of Cr, which more in quantity than the other three fruits. Pineapple and muskmelon juice also contain more amount i.e. 1.13 and 4.76ppm. but in Cucumber juice contain less amount i.e. 0.6ppm than other fruits juice. Therefore, Banana fruits bear more quantity of heavy metal with reference to WHO. Hence, it is not suitable for eating purpose.

The permissible limit of Fe is 0.80 ppm. All fruits juice are cross this permissible limit. Banana contains 13.26 ppm of Fe, which is high in amount than the other three juices. In these, also the Pineapple and Muskmelon juice contain 11.9 and 12.71 ppm, but Cucumber fruit are in less amount i.e.1.27 ppm than other fruits juice.

The permissible limit of Pb is 0.1ppm. all fruits juice are also cross these permissible limit. Banana fruit contain 24.4 ppm of Pb, which is high amount than the

other three fruit juices. Cucumber and muskmelon are also in more quantity i.e. 6.7 and 15.9 ppm but in Pineapple juice, Pb is less in amount i.e. 3.5 ppm.

The permissible limit of Cd is 0.06 ppm all fruits are above the permissible limit. In these Banana fruit also contain high amount of Cd i.e. 4.05 ppm while Cucumber, Pineapple and Muskmelon contain 1.59 ppm, 1.40 ppm, 2.88 ppm which is less in amount than banana juice.

The permissible limit of Zn is 15.0 ppm. Here, all fruits juice are crossed the permissible limit of Zn. In these, Banana fruit are also in high amount i.e. 43.32 ppm then Pineapple juice is 17.00 ppm which is also in more amount than Muskmelon and Cucumber fruits, they are less in amount i.e. 7.29 ppm and 2.32 ppm.

The permissible limit of Cu is 0.1 ppm all fruits juice are above the permissible limit of Cu. Here, Muskmelon Fruit contain more amount of Copper i.e. 6.28 ppm whereas Banana juice is 5.92 ppm of Cu is found. But in Cucumber and Pine apple juice contain less amount of Cu i.e. 2.34 and 2.28 ppm.

The permissible limit of Ni is 0.14 ppm. Ni is very low amount in all fruit juice, but it is cross the permissible limit according to WHO. As compared to four juice Banana juice contain more amount of Ni, than other juices i.e. 2.07 ppm Pineapple and Muskmelon juice contain 1.36 and 1.79 ppm of Ni. Cucumber juice contain very low amount of Ni i.e. 0.86 ppm.

Hence, above experimental study we conclude that, Banana fruits contain all heavy metals in more quantity except Nickel, which harmful for human beings for eating purpose. The intake of heavy metal contaminated fruits may cause risk of serious health effects.

Recommendations (Applicability)

There is growing awareness about the efficacy of essential elements in the maintenance of good health and prevention of diseases.

Zinc plays a vital role in wound healing, immune system, reproductive system and nervous system. Zinc wades off oxygen free radicals and also aid in metabolism of carbohydrates by assisting insulin to function.

Chromium lowers blood sugar and also works with insulin in metabolization of sugar, while copper is required for conversion of body's Fein to Haemoglobin.

Copper lowers low density lipoprotein (LDL) cholesterol, raises high density lipoprotein (HDL) cholesterol and preven toxidation of low dnsity lipo protein (LDL) cholesterol.

Iron is necessary for production of hemoglobin, immune functioning and drug detoxification. Manganese aids in maintenance of blood glucose level, synthesis of interferon, energy production and bone growth.

In this study **Pb, Cd, Zn, Cu, Ni, Fe** and **Cr** in selected traditional fruits growing/ found in Konkan region were determine during spectros copy.

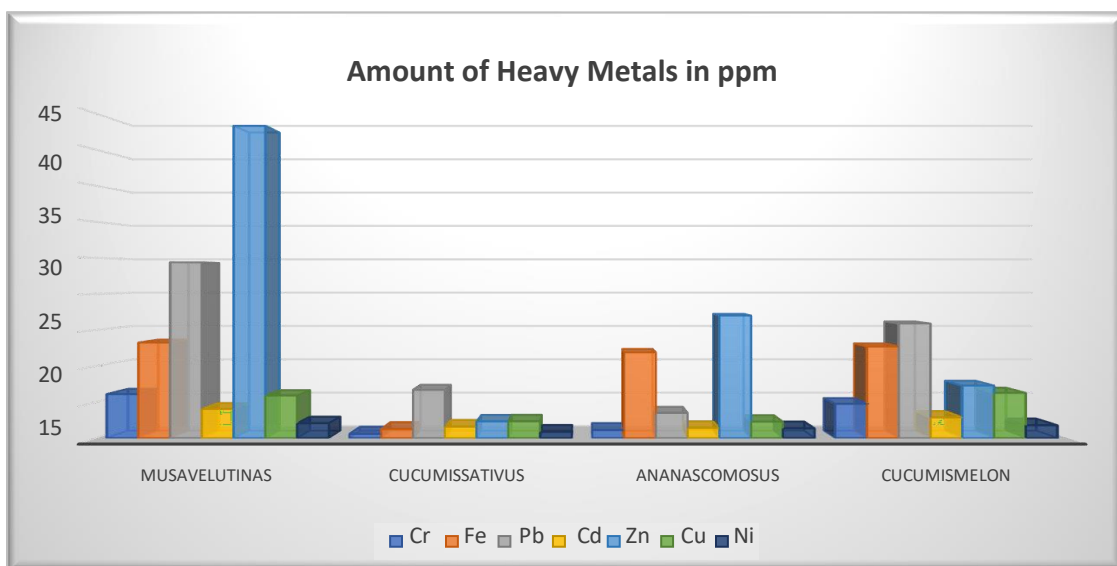
After sometime cool the solution and pour in 100 cm³ standard measuring flask and filter it using filter paper. Add 10 cm³ 2 N Acetic acid and dilute the solution to 100 cm³ using distilled water. This is as to ck solution of Muskmelon juice.

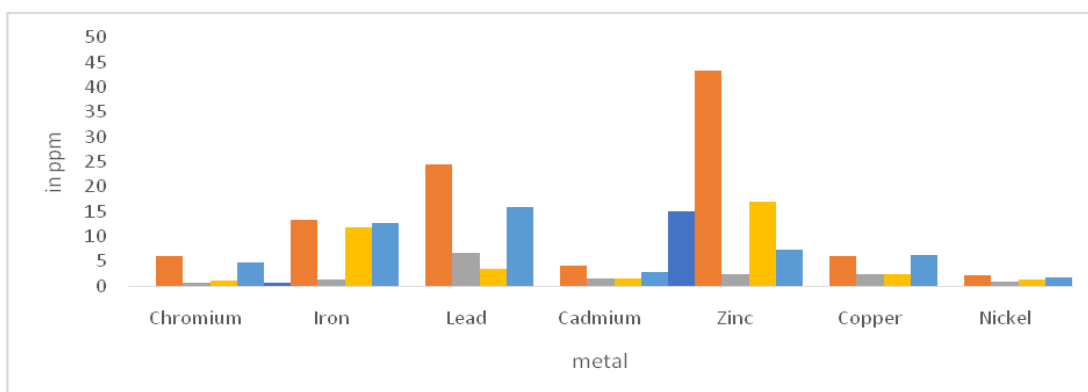
Iron is the most important mineral present in human body and also it is harmful even in excess amount for human being, the soil or plants also contain high amount of iron. The

iron is determined by spectrophotometric determination and measure the absorbance of solution at 520 nm against reagent blank. 10% 1, 10-phenanthroline is used as reagent and 10% Hydroxylamine hydrochloride is used to maintain pH and 2M Sodium acetate used in increasing amount. The red colored complex of Fe (III) is measured spectrophotometrically. Due to deficiency of iron causes anemia and if excess amount of iron causes death also metals are also present in Fruits in minute quantity. Though the presence of heavy metals in fruits is acceptable upto some level called as permissible level after that these metals may be hazardous to the animals which are dependent on the plants by in taking of leaves, grass, fruits We have been study in this project whether such local fruits have contained the heavy metals up to permissible limits or beyond the permissible limit which makes them in harmful category for the intake of human being as well as other animals.

The aim of this study is to analysis of this heavy metal content present in the regional fruits. To estimate the content of heavy metal and to check it is present in permissible limit or out it.

The Konkan region has various mining are as found. Geological survey of India reported incidence of less than 0.1 ppm gold in laterite and iron ore of Kalne area. Kalne is Maharashtra's only major iron ore extracting mine for an important reason. It is located in Sindhudurg, a region estimated to hold 90% of the states reserves of iron ore.





Conclusion

More recent findings globally have linked excessive bioaccumulation of heavy metals to numerous health abnormalities such as some forms of cancers, decreased intellectual capacity, and decreased reproductive health and cardio vascular diseases. In conclusion from this study the fruit species contained considerable nutritional value that may meet body needs. All the above findings (results) of fruit samples, are compared with the International Permissible Limit (IPL) of WHO as-

Elements in Fruit juice sample	Permissible Limit	Amount of heavy metal obtained in ppm			
		Musavelutinas	Cucumissativus	Ananascomosus	Cucumismelon
Chromium	0.05	6.11	0.6	1.13	4.76
Iron	0.80	13.26	1.27	11.9	12.71
Lead	0.1	24.4	6.7	3.5	15.9
Cadmium	0.06	4.05	1.59	1.40	2.88
Zinc	15.0	43.32	2.32	17.00	7.29
Copper	0.1	5.92	2.34	2.28	6.28
Nickel	0.14	2.07	0.86	1.36	1.79

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