COPPER IN CEYLON TEAS

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Copper is one of the elements essential to the normal functioning of life processes, its role in the formation of haemoglobin in the liver of vertebrates and in the cell respiration of plants is well known. The activity of a number of oxidising enzymes* isolated from vegetable sources is prevented in the absence of this element in the enzyme system. Tea polyphenol oxidase belongs to this group of enzymes and consequently enzymic copper in tea leaf is essential for the oxidation of tea polyphenols during fermentation. A direct relationship has been found to occur between the amount of enzymic copper and the rate of fermentation (Norris, 1944). Purified enzyme preparations have also shown a direct relationship between their activity and the copper content (Sreerangachar, 1943).

Stage of purification		*Polyphenol oxidase activity relative to green leaf*	*Copper content of the enzyme preparations (p.p.m.)*
1	...	151	32
2	...	330	60
3	...	3100	267
4	...	5060	625
5	...	10100	800

It has been found that in Ceylon teas about a third of the total copper in the leaf is present in the polyphenol oxidase. Teas deficient in enzymic copper do not ferment properly. Regular spraying of copper on the tea bushes is being carried out in parts of Nyasaland to make good a deficiency in this element.

As a matter of interest a non-fermenting clone (TRI Clone 9) has been propagated by the Plant Physiology Division of the T.R.I. and this has been found to be deficient in enzymic copper. The physiological characteristics of this clone are such that it is incapable of absorbing sufficient copper from the soil for the formation of the copper-protein enzyme, polyphenol oxidase. Injection of copper to the bush, or dipping the shoots in copper sulphate solution, increased the enzyme content, sometimes by five or six times, depending upon the concentration of the copper sulphate solution and the period of dipping. Fermentation of the treated leaf was then found to be normal, but the infusions were green due to the absorption of copper by the chlorophyll. Copper in the chlorophyll increased from the normal 5 up to 32 parts per million (p.p.m.). It is notable that addition of inorganic copper to the crushed leaf had no effect on fermentation, and evidently copper must be absorbed by the living cell if the copper-protein enzyme is to be produced. (Norris, 1944; Lamb, 1945).

*_Enzyme_. If coal gas and air are mixed, normally nothing happens unless high-temperature heat is applied—a flaming match or a hot glowing wire; but a small area of platinum black, cold, will ignite the mixture. The platinum black is a *catalyst*. An *enzyme* is a sort of biological catalyst. All chemical activities in animals and plants are mediated by enzymes, from the building-up of starch in leaves to the energetic display of a champion hurdler. There are many different kinds of enzymes—all produced within living animals and plants. They are themselves complex chemicals and none have yet been made by non-living processes.

Analyses for copper content of tea flush from a number of clones propagated at the T.R.I. showed a variation between 16 and 30 parts per million (Lamb, 1948). The buds contain more than the leaves, whilst the stalks contain the least amount of copper.

Parts of the flush	*Copper content (p.p.m. dry wt.)*
Bud	33
1st Leaf	25
2nd Leaf	26
Stalk	19

This variation in the copper content of the parts of the flush is reflected in that of the various grades of tea. The fannings grade which contains most bud and least stalk, shows the highest amount of copper.

Grade of made tea	*Copper content (p.p.m. dry wt.)*
B.O.P.	24
F.P.	24
B.P.	24
B.M.	24
B.O.P. Fannings No. 1	31
B.O.P. Fannings No. 2	31
Dust No. 1	30

The copper content of made teas from different tea-producing countries varies considerably. The results of analyses of different grades and blends of tea available in the T.R.I. collection of foreign tea samples are shown below:

Tea producing country/Blend	*Copper content (p.p.m. dry wt.)*
North India-Assam, B.O.P. ...	31
North India-Assam, Fair B.P.	35
South India-Travancore, Good B.O.P. ...	34
South India-Travancore, Fair B.O.P. ...	31
Ceylon, Good B.O.P.	19
Ceylon, Fair B.O.P.	26
Japan, Low Black	62
Formosa, Good Oolong	18
Nyasaland, Average B.P.	25
Nyasaland, Good B.O.P.	24
Brooke Bond's blend	32
Co-op. special blend	27

During manufacture, the copper content of teas increases slightly, particularly during the rolling process because of contamination from the brass fittings. The increase is very much less in wooden rollers (with only a few brass parts) than in brass rollers (consisting of brass jacket and table).

Stage of Manufacture		*Copper content (p.p.m. dry wt.)*	
		Wooden rollers	*Brass rollers*
Withered leaf	...	23	23
1st Dhool	...	24	33
2nd Dhool	...	24	34
3rd Dhool	...	23	37
4th Dhool	...	25	34
Fired Tea (Bulk)	...	27	34

About a quarter to a fifth of the copper (inherent) present in made tea is soluble in the 5-minute brew, representing 0.09 to 0.12 parts per million of copper in the liquor.

Sample No.	*Copper content of tea (p.p.m. dry wt.)*	*Solubility of copper in the 5 min. brew*	*Copper content of the tea liquor (p.p.m.)*
1	26	22.0%	0.09
2	27	24.4%	0.11
3	30	21.0%	0.10
4	34	21.5%	0.12

Since the introduction of copper fungicides spraying for Blister Blight, copper residues have inevitably found their way into made tea. The authorities of some importing countries (notably the U.K. and U.S.A.) will not permit more than 150 p.p.m. of *total copper* in made tea. Routine analyses of made tea are carried out by the Government Analyst, Colombo, and the following table summarises the results from February, 1953, to November, 1959.*

Range copper content in (p.p.m.)	*Tea samples falling within the range*	
	Number	*Percent of samples*
0 – 10	4	0.3
11 – 20	22	1.5
21 – 30	75	5.1
31 – 40	165	11.2
41 – 50	214	14.5
51 – 60	239	16.2
61 – 70	212	14.4
71 – 80	184	12.5
81 – 90	142	9.6
91—100	91	6.2
101—110	62	4.2
111—120	37	2.5
121—130	14	1.0
131—140	4	0.3
141—150	3	0.2
151—160	2	0.1
161—170	1	0.1
171—180	3	0.2
181—190	0	—
191—200	1	0.1

It may be seen from the above results that over 90% of the tea samples showed a copper content of less than 100 p.p.m., while over 99% of the samples contained less than 150 p.p.m. copper. It should, however, be stressed that whenever the

* By kind permission of the Tea Control Department, Colombo.

copper content of any particular invoice rises above 100 p.p.m., the estate concerned is informed and is advised to bulk such teas with teas of lower copper content so as to bring the copper content of the bulk to below 100 p.p.m. It would of course, be very unusual for one invoice to be packaged without a great deal of blending.

Although the spraying operations are carried out during the heavy monsoon season, and therefore most of the sprayed copper is washed off by rain, a fraction of it is always tenaciously held by the leaf. It has been found that even when the leaf is sprayed with soluble copper salts (*e.g.* copper sulphate), and immediately washed thoroughly with water, a fraction of the copper is still held by the leaf.

Treatment	*Copper content (p.p.m. dry wt.)*
1. Control	17
2. Leaf sprayed with copper sulphate and immediately washed thoroughly with distilled water ...	27
3. Leaf sprayed with copper sulphate but not washed	86

The exact nature of this capacity of the tea leaf to retain copper is still not known. Results of preliminary experiments have however indicated that chlorophyll takes up part of the copper to form copper-chlorophyll. Pectic substances in tea leaf are also likely to combine with copper to form copper pectate.

It has been shown earlier that about 20 to 25 per cent of the copper present in teas made from unsprayed leaf passes into the liquor; the solubility of the copper (inherent plus the residual) present in teas made from sprayed leaf (copper fungicides), on the other hand, showed a variation between 7 and 27 per cent, depending upon the strength of the brew and the copper content of the made tea. The per cent solubility was not affected appreciably by the period of brewing, between 5 and 30 minutes. A few typical solubility results are shown below:

Amount of copper which enters the liquor with weaker tea (2.7g in 170 ml.) and stronger tea (3.7g in 170 ml.), with black tea containing various proportions (p.p.m.) of copper and therefore various amounts (micrograms) per brew.

Brew	*p.p.m.*	*Micrograms per brew*	*Micrograms in the liquor in 170 ml. (one cup)* 5 & 10 min.	15 & 30 min.
Weaker ...	222	599	114	111
	160	432	60	55
	111	300	52	49
	44	119	32	30
Stronger ...	222	821	132	108
	160	592	45	43
	111	411	48	41
	44	163	31	29

The stronger brew does not contain more copper than the weaker, but when the black tea has more copper in it, more got into the liquor. This is somewhat mysterious, but in any case, the largest amount found was 0.8 p.p.m. In fact, of course, the black tea must not have more than 100 p.p.m. which gives about 0.3 p.p.m. in the liquor. This is lower than in other ready-to-drink beverages such as cider, beer, stout (0.5 to 2.0 p.p.m. copper), and wines (2 to 10 p.p.m. copper). It is of interest to compare this low copper content of tea liquors with that found in many food products which are consumed either partly or wholly:

Food product		*Copper (p.p.m.)*	*Reference*
Banana	...	2.0	(Nicholls, 1945)
Cereals	...	3.5	do.
Cheese	...	0.2	do.
Chestnuts	...	6.0	do.
Chocolate (bitter)	...	26.7	(Winton & Winton, 1939)
Cocoa	...	33.4	do.
Coconut	...	7.0	(Nicholls, 1945)
Coffee	...	24.0	(Winton & Winton, 1939)
Eggs	...	2.5	(Nicholls, 1945)
Fish	...	2.0	do.
Fruits	...	1.0	do.
Fruits (dry)	...	3.5	do.
Honey	...	2.0	(Winton & Winton, 1939)
Liver (Beef)	...	44.0	(Nicholls, 1945)
Liver (Calf)	...	22.0	do.
Meats	...	1.5	do.
Milk	...	0.2	do.
Nuts	...	12.0	do.
Oysters	...	30.0	do.
Poultry	...	3.0	do.
Pulses	...	7.0	do.
Vegetables	...	1.0	do.

In conclusion, copper, which is one of the essential elements for the life processes of vertebrates and higher plants, is required for the formation of the copper-protein enzyme in tea leaf responsible for the oxidation of tea polyphenols during fermentation. The amount of copper consumed in tea liquors is very minute and not likely to be injurious to human health; on the contrary it is likely to be beneficial.

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