Determination of fluoride in tea by ion selective electrode

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ABSTRACT: Tea leafage is very plenty in fluoride, since tea herbs keep in fluoride from the clay and accumulate in its plenty. Some of this fluoride is released into the infusion, which is pissed as a tea. Fluoride is present in tea could be handy for the forestall of dental caries, however, it may result in undue entrance and lead to enamel fluorosis. The purpose of this review was to collect the other researchers work about determination the fluoride levels in different brands and types of tea by means of a computer-controlled ion-selective electrode potentiometry used a different method.

Keywords: Tea, Fluoride, Ion selective electrode

1 Introduction

One of the halogen element is Fluorine and it is known the very reactive non-metal. Its properties and chemical behavior are mainly unlike from elements of halogens. Fluoride is momentous anion which emerge in various environmental, food samples and clinical. Fluorine is both useful oligo element (necessity for bone tissue and teeth growth and upholding) and venomous (for matures the fatal dose is 0.20-0.35 g F− per kg body weight) [1] upwards of F− concentration in the humanistic body can be the outcome of living in make dirty environment and nutrition with contaminated food. Higher fluoride entry, above recommended levels (1.5 mg L−1), leads to skeletal and dental fluorosis [2,3]. Acute fluoride intoxication can have neurological complexity [4] formation urinary stone [5] and hypocalcaemia [6] as emphasis on regional patients. Nowadays published documents was described a contact between fluoride intake and cancer [7-10]. Tea is also considered a major source of fluoride, since tea herbs (Camellia sinensis) pick up fluoride from the clay and accumulate in its leaves. Epidemiological surveys have recorded that some populations who drink tea on an orderly basis have a reduced number of flimsy teeth [11, 12]. On account of the fluoride content, tea should be an effective vehicle for delivering fluoride to the verbal gap helping to forestall dental decay. During latest years varied papers have been published on the fluoride ingredient of tea leafage [13-15]. However, the results acquired are often in poor agreement. The accuracy and precision the of the analytical method used may give the contribution on the variation of the results. Miehe and Feldheim [11] reported the total fluoride ingredient in tea leafage to range from 40 to 330 mg L−1[16]. They also reported that the ultimate fluoride contents are found in subdued leaves. Fluoride accumulated in young leafage ranged from 250 to 300 mg/kg and old leafage over 2000 mg/kg. Some of this fluoride is released into the vaccination, which is drunk as tea [11] reported the fluoride concentration in decaffeinated and caffeinated tea vaccination ranged from 1.01 to 5.20 mg/l and 0.34 to 3.71 mg/l, respectively. Based on the reported fluoride content from black teas, the advantages of fluoride in tea specially for children have been discussed. Some novelists agree that fluoride in tea is advantageous since it could account for an important portion of total dietary fluoride intake. On the other hand, the fluoride in tea may
result in ultra-entry and lead to glazing fluorosis. Fluoride may cause dappled teeth at around 1 mg/l when it is existing in water. For that motive, the determination of fluoride ingredient as a trace element in tea vaccinations is important in order to detect any probable health hazards. Determination of fluoride in tea is generally executed by direct potentiometric techniques using an ion-selective electrode. The computation of the outcomes is acquired using a regulation curve, which provides that the electrode potential is linear arrangements to the logarithmic of the ionic activity. It is a simple procedure without any exemplary preparation for measuring aqueous samples. However, any problems appear when the pattern matrix is complicated, such as tea that includes vitamins, volatile oils, polysaccharides, minerals, purines, alkaloids, and polyphenols. In this situation, the electrode potential is frequently not linear to the logarithmic of the ionic activity because for the conflicting molecules and the fluoride contents may be discovred to be somewhat lower than the levels in real samples [17].

Tea

Tea is one of the most use up beverages of the world. At the Present time, it is wrought in at minimal 30 countries around the world. Tea beverage is an inclusion of the dried leafage of *Camellia sinesis*, a agency of Theaceae family. It is an every time green tree or shrub that can grow up to an altitude of 30 feet, however is usually cropped to an altitude of 2.5 feet in breeding. The shrub or tree is heavily branched with dark-green, oblong, hairy, ovate leafage cultivated and preferentially picked as young shoots. Older leafage are aforethought to be subaltern in quality. Freshly spare tea leaf is processed differently in different parts of the world to give oolong tea (2%), black tea (78%) or green tea (20%) [18]. Green tea is available from the crisp tea leaf and thoroughly consumed in China and Japan. Western ethos favor black tea which is available through the oxidation, heal process of maceration and display to atmospheric oxygen [19, 20]. The expenditure of olong tea is mostly confined to Taiwan and China, as well roasted tea is consumed mostly in Japan. roasted and Green teas are respectively, steamed, to prevent from enzymatic oxidation; oolong tea is semi leavened to consent a moderate grade of enzymatic oxidation pending processing [21,22]. Also, *Ilex paraguayensis* is a species of tea from South of America. This herb is processed to acquire a final trading product named yerba mate. The mate is a renowned popular tea use up in Paraguay, Argentina, Uruguay, and Brazil. Even though the therapeutic properties of yerba mate have been extensively explored, there are few studies of chemical composition of mate [23,24]. ‘Healthy Foods’ ingredient active scavengers of free radicals are most popular nowadays. Advertisements in newspapers and magazines regarding a “Wonder Cure” that prevent damage to the body are becoming ubiquitous. It is properly accepted that phenolic compounds included in certain foods have potential welfare benefits. Tea is addicted to helpful effects on human welfare with the polyphenols as the liable constituents [25, 26] Tea leafage as well as the resulting beverage tea are known to possess great quantities of polyphenols, particularly flavanols, the so called catechins 5,10. Many in vivo and in vitro effects of tea polyphenols have been reported [25, 27, 28] including anticarcinogenic, hypolipidemic and antioxidant properties.

### 2.1. Chemical composition of tea

In making verdant tea, the tea leafage are heated to inoperative the enzymes and dried. In this way ingredients of the tea leafage are protected in the dried tea leafage. When the tea leafage are leavend, for example 2.5 g in 250 ml of hot water for 3 minutes, about 30% of the strict materials are extracted into liquid. The spray-dried powder of the water extract, known as verdant tea solids, animal experiments used verdant tea solids for some requirements. All teas are contain numerous amount of polyphenolic compounds which are also present in fruit, vegetables, and red wine [29]. Fresh tea leafage is contain in water soluble polyphenols, specially flavanol gallate, flavanol glycosides and flavanols [30,31]. The major tea catechins: α-epigallocatechin (EGC), α-epigallocatechin-3-gallate (EGCG), α-
epicatechin-3-gallate (ECG), α-epicatechin (EC), α-epicatechin (EC), α-epicatechin-3-gallate (ECG) α-gallocatechin and β-catechin; constitutes 30% to 42% of the green tea solids by weight. Caffeine amounts for 3% to 6%. The constraction modify with the growing conditions and following processing of the tea. Black tea (‘Black’ used in this context be linked merely to the method of blade cultivation and not to the arbitrary addition of milk to the potable before consumption) is manufactured from fresh green leafage by ‘enzymatic browning processes (driven by coupled chemical oxidation and polyphenol oxidase) and of the flavanol gallates and flavanols and, to smaller extent, the flavanol (especially myricetin) glycosides and the non-flavanoid theagallin. These transmutations make an innitable range of tint including the red-orange theaflavins and brownish thearubigins, and theaflavins and theaflavic acids, as reviewed by Balentine and Harbowy [32]. The major polyphenols of black tea leafage and beverage are thearubigins. Their ingredient has been diversified estimated as 3-6%.

2.2. Antioxidant property of tea

In human organism, different preservation mechanisms are present to fight free radicals. there is also equilibrium between antioxidant and pro-oxidative process, and when this stability is disturbed in favour of oxidation stress results and free radicals, [33]. Lipoproteins when oxidized plays a significant role in the improving of atherosclerosis by means of oxidation process, low density lipoproteins (LDL) of walls in vascular. LDLs are very wealthy in cholesterol causing vary in structure of vascular walls. These structural modifications give a fillip to macrophages to agglomerate the oxidized LDL, promoting a vary into foam cells. These cells collected in the vascular walls leads to the first noticeable vary of cellular tissue, called fatty streaks. These varies can result in the total closure of the artery, which could cause vascular occlusion or angina. It is well established that other pathological states such as ischaemic reoxygenation, rheumatoid arthritis, cancer and injury of the liver and other organs, are set of by oxidation processes [34]. The very reactive antioxidant properties of the tea are generally attributed to its flavonoid components; bisflavanols, theaflavins, and theaflavic acids [35]. These compounds are all powerful antioxidant in vitro when consumed, may act as the free radical sweater which eject endogenously generated peroxyl, hydroxyl radicals ,and superoxide. The antioxidant feature of tea is also insider with a few other mechanisms e.g. formation of depolarization of electrons and intramolecular hydrogen bonds [36], rearrangement of the molecular structure [37]. These compounds may also prohibit oxidative reactions by chelating iron and free copper, whichever may catalyze the formation of reactive oxygen species in vitro [38,39].

2.3. Anticancer property of tea

Many case-control, epidemiological, and multitude studies have been directed to investigate the influence of tea expenditure on human cancer effectiveness, and this topic has been reviewed by several authors [40–43]. In a Japanese multitude study, devised a negative unification between total cancer incidence and green tea expense, especially amid females drinking more than 10 glass per day [44]. The influence of tea on stomach cancer has been the most widely studied. of 15 studies, five case control studies showed a protective impact of tea on the risk of stomach cancer [45–48]. A few studies have been done on drinking tea and colorectal cancer, with ineffective or no evidence of an fraternity. A novel study on middle aged Finnish men demonstrate a positive merger between increased colon cancer risk and green tea expense [49]. On the other hand, the sequel with green tea indicate a preventive effect of tea a large study of pancreatic and rectal colon cancers indicated decreased scenes of these cancers with outlay of tea [47]. The outcomes from the epidemiological studies concerning lung cancer and tea intake are unclear cause smoking agent was not taken into count in the study design. There is also some proof that green tea polyphenols have a chemopreventive effect against cancers in smokers [50]. The periodicity of sister-
chromatid barter in lung cells was lower in smokers who consumed green tea. In a seven-year give chase study of patients with breast cancer, it was found that increased sequel of green tea was united with decreased numbers of axillary lymph node metastases especially among premenopausal patients with stage I and II breast cancers [51]. premature studies have addicted tea drinking to both decreased and increased hazards of esophageal cancers, but latest studies have shown that the positive association between esophageal cancer and tea was because of the upper temperature at which the tea is spend. inventioning from the largest study of esophageal cancer conducted in China suggested that, barring the effect of drinking green tea, temperature decreases the hazard of esophageal cancer [52]. The anti-carcinogenic activities of tea polyphenols are generally depended to be concerned to their antioxidative properties. Tea may influence the metabolism of carcinogens by prevention of diversified cytochrome P450s or induction, however the practical stature of this mechanism is unknown. Amid the phase II enzymes, tea increases glucuronyl transferase action, which may facilitate the detoxification lane of definite carcinogens. Obstruction of tumor promotion-related enzymes, like lipoxygenase and cyclooxygenase [53, 54] ornithine decarboxylase [55-57] protein kinase C [58].

2.4. Fluoride

Fluorine has the anionic form is called Fluoride. It is an important anion, since a minor amount of fluoride has helpful effects on the teeth by reducing the proportion of caries [59]. Hydroxyapatite interacts with fluoride by replacing the hydroxyl ions to create a new more crystalline phase. This phase called fluoroapatite, is lot resistant to washout by license plate acid and represents a lower surface energy thus making licence plate adhesion more inconvenient [60] Fluoride may also rising up the rate varnishl remineralization, so that phosphate and calcium ions are screened and not lost during demineralization. Moreover, fluoride may remove the metabolism of bacteria in license plaque or oral concentration of cariogenic bacteria. For this occasion, the inlet of fluoride is required to support great dental health. fluoridated drinking water in some countries appear to be the major dietary welding of fluoride, and the ideal quantity of fluoride for prevention of dental caries has been proposed as 1.0 ppm. Fluoride has both detrimental and beneficial effects on human bodies health. In conditions of dental health, the generality of dental caries is upside down concerned to the concentration of fluoride in drinking water; duration there is a dose-response relationship between the universality of dental fluorosis and the concentration of fluoride in drinking water. In situation of general health, in societies where foodstuffs and drinking water are extremely high in fluoride, Bone fracture and skeletal fluorosis are the most suitable contrary effects. However, there are also other sources of fluoride. The aetiology of dental caries involves the interplay on the tooth surface between certain oral bacteria and simple sugars (e.g. sucrose) derived from the diet. In the shortage of those sugars in drinks and foods dental caries will not be a generic health problem. However where sugar expense is increasing or is high, dental caries will be or will become a substantial generic health problem except there is suitable intervention [61].

2.5. Ion Selective Electrode

An ion-selective electrode (ISE) is sort of an indicator electrode that reply (propagate a potential) when it is establish in a solution having a certain ion. There is presently a large variation of ion-selective electrodes existing which selectively respond to special cations and anions, and definite gases; pH electrodes are by remote the best known. These may be operated for many diverse applications and novel in chemical analysis. All ISEs have an elementary likeness in their design: the ion-sensing part consists of a membrane (which perhaps glass, plastic or an ionic crystal) which has sites which are capable of adsorbing the analyte ion. On either side of the membrane is a solution including the ion of attention: one of these is the test solution, and the another is a standard solution within the electrode itself. Inside
the electrode body there is an electrical connection a reference electrode or a wire to follow up the response from the membrane. This is shown in Figure 1 [62].

![Figure 1](image)

**Figure 1** Basic structure of any ISE.

The ion-sensing membrane has sites on each surface where the analyte ion can bind in an equilibrium process: the higher the concentration of ions in solution, the more sites will be occupied. When the electrode is placed in a different solution, the number of adsorbed ions will change. This does affect the new solution, but by an undetectable amount [63].

![Figure 2](image)

**Figure 2** Ion-sensing membrane (x is analyte ion).

2.6 Applications about the determination of fluoride in tea by Ion Selective Electrode

The fluoride content of coffee and tea as normally brewed, and after Schoniger oxygen flask combustion, has been determined with a fluoride ion-selective electrode paired to a microprocessor analysis in two of its operating modes. Up to forty samples per hour can be assayed in the CONCN mode and the results compare favorably with the known addition (KA) back-up mode. A group of researchers researched to determine the content of fluoride in Iranian dark tea and tea liquor. Ten of the most thoroughly use up brands of black tea in Iranian were bought in from regional bazaar markets. Four to nine samples (60 altogether) of each brand were gathered and analyzed. F– concentrations in the tea and tea vaccination were determined by the method of Duckworth and Duckworth with a F– ion selective electrode (ISE) calibrated against a standard sodium fluoride solution in deionized water. For determining F content in tea, a weighed 0.1-g sample of tea, dried at 60°C for 5 hr was mixed with 3 mL of 0.1 N NaOH in a nickel crucible which was placed in an oven at 150°C for 2.5 hr. After the water was vaporized, the crucible was heated in a muffle furnace at 300°C and then 600°C for 30 min. The sample was consent to chilly and supplementary 5 mL of distilled water. thereafter 3 mL of 37% Hydrochloric acid HCl was added to regulate the pH to 8-9, and the sample was adapt to a 100 mL volumetric flask to which an equal volume of total ionic strength adjustment buffer (TISAB) was supplementary. The solution was diluted to the sign with distilled water and filtered owing to Whatman Number 40 filter paper 5. The TISAB solution was make by dissolving 22.05 g of 'sodium citrate dehydrate' and '0.8 g of sodium hydroxide' in deionized water and diluting to 100 mL. After that the pH was regulate to 5.3 with 'perchloric acid'. To each 2.0 g pattern of tea dried as afore, the Iranian mode of tea vaccination was performed by extension of 50 mL of boiling deionized water and the mixture hold at 80°C on a water bath for 5–20 min (usually 10 min). At the end of the vaccination period, the tea eject was diluted to 100 mL with deionized water, and the F– concentration was determined by the ISE method [64].

During 2007 a group of reserarcher researched about Determine fluoride level in tea beverage by Ion Selective Electrode [65] Potentiometric analysis of fluoride ingredient (as F– ion) in solutions by using fluoride ion-selective electrode is simplistic, dependable and low cost. Very petty concentrations of fluoride-ions (to 10–6 mol/dm3) can be determined by fluoride selective electrode, with arrangement of ion force of a solution and inspection of concentration of hydroxide ions and conflicting ions of metals. The action of pH and
complexing ions of metals can be prosperously concerted by the TISAB solution and by keeping pH value in the series from 5.00 to 7.00. The present of fluorides in the samples can be specify by the method of direct potentiometer, and in the case of very nominal concentration by standard addition method. In him paper it was analyzed fluoride ions concentration in tea, by using the fluoride selective electrode. The admitted conclusion from the analysis of fluorides in teas represent that fluorides exist in teas in different concentrations. There are also differences between the same kinds of tea, which is noted with mint (\textit{Mentha piperitae folium}), as a consequence of differences between soils where it was planted.

Determination of fluoride in Tea lefage and Tea vaccination by Ion Selective Electrode by [66] A fluoride ion selective electrode method for the determination of fluoride present in tea lefage and tea vaccination was establish. Using vocational timothy sod powder and tea leaf powder as standard materials, this method demonstrated linearity between 0.02 and 2.00 mg/L of fluoride with R2 greater than 0.999. Both materials had coefficient of variations (CV, %) less than 3%, indicating good reproducibility in the determinations. The salvage tests of tea vaccinations spiked with different amounts of ‘sodium fluoride’ demonstrated 94-106% of salvage with CV less than 1.2%, representing that the method is very accurate. With 1% of tea greenery to boiling water ratio, as much as 64-78% of fluoride in tea lefage could be released into tea vaccination by repeated vaccination and 82-84% by continuous infusion. By this process, aggregate fluoride contents of 12 brands of tea lefage acquired from Nantou County were determined to be 100-451 mg/kg dry weight, and those of their infusions in boiling water for a 5 min period were determined to be 0.39-1.21 mg/L. On the assumption that daily tea vaccination drinking 2 L for by an adult, fluoride entry from tea vaccinations of these tea lefage is far below the daily fluoride bearable upper limit 10 mg.

Another group of researcher researched [67] The fluoride content was analyzed in 43 tea infusion. The peruse patterns were the mints “\textit{family Lamiaceae}, lemon balm “\textit{Melissa officinalis}” and the mint “\textit{Mentha piperita}” and, pomegranate “\textit{Punica granatum}” and green tea “\textit{Camellia sinensis}” and in tea bags, bulk purchased and bottles in regional marketplaces and supermarkets in Croatia, Split, were determined. Potentiometric determination of tea by handling fluoride ion-selective plate was operated in this work. Mean F\textsuperscript{−} concentration in all tested samples was 0.116 ± 0.211 mg L\textsuperscript{−}1. In commission to get a better grip into the fluoride content in different herb samples, a One-road ANOVA programme was usage for statistical datum analysis. Concentration of F\textsuperscript{−} follow up log-normal distribution with factors dispensation of mean concentration value of 3.77 mg L\textsuperscript{−}1 and alteration 3.00 mg L\textsuperscript{−}2. F\textsuperscript{−} concentration was advanced (\textit{P} < 0.001) in vaccination of verdant tea (0.23 ± 0.393 mg L\textsuperscript{−}1) than in vaccination of mint (0.011 ± 0.004 mg L\textsuperscript{−}1) and pomegranate tea (0.002 ± 0.008 mg L\textsuperscript{−}1). On the other side, F\textsuperscript{−} concentrations (\textit{P} < 0.001) were inferior in stack samples (0.003 ± 0.008 mg L\textsuperscript{−}1) than tea beverages (0.116 ± 0.161 mg L\textsuperscript{−}1) and in tea bags ones (0.259 ± 0.164 mg L\textsuperscript{−}1). F\textsuperscript{−} content was statistically different among same herb samples in correlation of samples packing. For verdant tea samples (\textit{P} < 0.001) F\textsuperscript{−} concentration was lower in bottled verdant tea beverage (0.12 ± 0.161 mg L\textsuperscript{−}1) than in tea bags (0.12 ±0.558 mg L\textsuperscript{−}1) than they have got same situation for pomegranate tea samples, in tea bags (0.0020±.00921 mg L\textsuperscript{−}1) and bulk ones (0.002 ± 0.00713mg L\textsuperscript{−}1) respectively. For mint tea samples they did not find correlation between F\textsuperscript{−} concentration and sample packing.

3 Conclusion

Maximum of finding fluoride concentration in analyzing samples is about 3 times lower than the maximum allowed daily intake (0.558 versus 1.5 mg L\textsuperscript{−}1). Green tea samples have significantly higher fluoride concentration compared with ones for mint and pomegranate tea what was expected, according information about fluoride accumulation in green tea. We found the effect on the sample’s package on fluoride levels, but only for green tea samples. Higher levels were found in tea samples packed in tea bags.
than in bottled ones, for green tea sample concentration in tea bags was 0.558±0.12 mg L⁻¹ and in bottled green tea beverage was 0.161±0.12 mg L⁻¹. Results show that F⁻ concentration depends both on brewing time and leaching fluoride from tea, but does not happen in the same way. Would fluoride concentration increase or decrease, it depends on how fine are plant cuttings (in fact on specific surface and for smaller cuttings it would be greater) and on the country of origin, soil type, respectively. According the results, we would not suggest anyone drink a tea after 24 h of preparation, especially green tea, because fluoride concentration can be very high and/or above the recommended maximum daily intake of fluoride. In the normal way of thinking, for testing samples, people would obey manufacturer’s recommended procedure for tea preparation and assure themselves of possible fluoride poisoning.

References


Competing Interests:
The authors declare that they have no competing interests.

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