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Fluoride Content in Tea and Its Relationship with Tea Quality

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The tea plant is known as a fluorine accumulator. Fluoride (F) content in fresh leaves collected from 14 plantations in China was investigated. The F increased with maturity, and the F variation was remarkable in the tender shoots. Furthermore, significant negative relationships were observed between F content and the content of the quality parameters total polyphenols and amino acids. These substances are rich in young leaves and poor in mature ones. With regard to quality of tea products, the relationship with F content was studied using 12 brands of tea products in four categories: green tea, oolong tea, black tea, and jasmine tea collected from six provinces. The F level increased with the decline in quality and showed good correlation with the quality grades. The results suggest that the F content could be used as a quality indicator for tea evaluation.

KEYWORDS: **Tea; *Camellia sinensis*; fluoride; polyphenols; amino acids; quality**

INTRODUCTION

Tea became one of the most popular beverages in the world because of its favorable taste, aroma, and health-promoting effects. About 3×10^9 kg of various teas is consumed every year. In the tea trade, the price is quite variable depending on the quality. The quality of tea is very important.

The quality grades of tea are determined by sensory evaluation performed by specialists. In China, the made teas are usually classified into about six grades depending on sensory qualities, such as maturity, shape, color, brightness, aroma, and taste. The tea of grade 1 has the highest quality; the grades following are ranked as grade 2, grade 3, and so on. Tea with the quality higher than that of grade 1 is ranked as super grade.

Attempts have been made by tea researchers to explain tea quality chemically and to develop chemical and physical methods for evaluating tea quality. Polyphenols, caffeine, amino acids, and total water-soluble solids have been confirmed to contribute significantly to the taste and flavor of made tea (*1*, *2*). There is a concurrent decline in these quality parameters and the quality of the made tea with the increase of the maturity of the tea shoots (*1*, *3*, *4*). Therefore, the maturity of fresh leaves is an important factor in the quality of made tea. That is why the level of crude fiber, the content of which in fresh leaves changes significantly with maturity, has been listed as one of the quality parameters in the ISO standard (*5*), although it has no direct relationship with the taste or flavor of the made tea.

The tea plant (*Camellia sinensis*) is known as a fluorine accumulator. It has been observed that fluoride (F) content in tea leaves may be 1000 times the water-soluble F and 2−7 times the total F content in the soil (*6*). F absorbed from the soil forms F−Al complexes, transports the Al to the leaves, and then transfers the Al to catechins (*7*). Most of the F accumulated in leaves is in the form of the F anion (*8*). It is reported that the leaves contained nearly 98% of the F of the whole plant (*9*), and the most was accumulated in old leaves (*10*-*12*). Because F in tea is easily released in tea infusion, tea can be a major source of F (*6*). There are also papers focused on the bioactivities of F in tea, such as the prevention of dental caries in small amounts (*13*, *14*) and the cause of fluorosis after long-term overexposure (*15*), etc. The F content in brick tea, which is made from old leaves and branches, has also been discussed (*11*, *12*, *16*). The research showed that brick tea contained a higher F content than other types of tea, which are made of young tender shoots. However, little information has been found concerning the relationship between F level and tea quality.

The present study was undertaken to quantify the F variation in fresh leaves and to assess the relationships of F content to other constituents and to the quality of made tea.

MATERIALS AND METHODS

Materials. Fresh leaves of *C. sinensis* were collected from 14 plantations in Fujian, Guangdong, Hunan, Hubei, Jiangsu, Sichuan, Yunnan, and Zhejiang provinces, which are the main tea production provinces in China, covering the eastern, southern, and southeastern regions, respectively. The young shoots of the six plantations in Zhejiang and Fujian provinces were divided into bud and first leaf, second leaf, third leaf, fourth leaf, fifth leaf, and sixth leaf, respectively. The fresh leaves were steamed for 3 min and then oven-dried at 80 °C for 8 h.

The made teas, including five brands of green tea (unfermented tea), two brands of oolong tea (semifermented tea), three brands of black tea (fully fermented tea), and two brands of jasmine tea (green tea scented with jasmine flowers), with different quality grades were the standard samples for sensory evaluation provided by the tea factories from six provinces.

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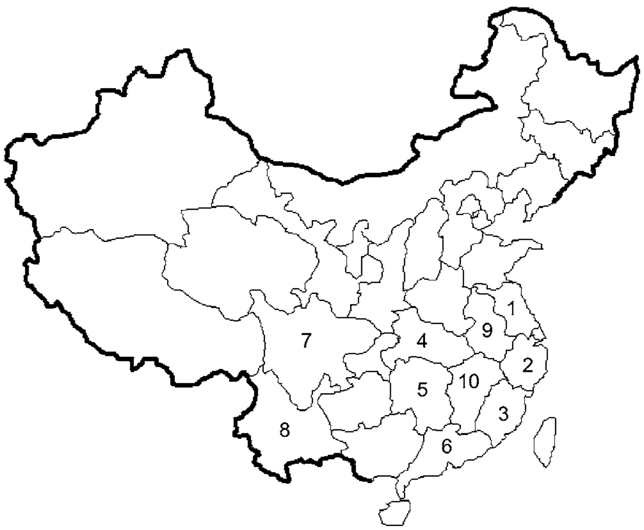

Figure 1. Sampling areas of tea leaves and tea products: 1, Jiangsu; 2, Zhejiang; 3, Fujian; 4, Hubei; 5, Hunan; 6, Guangdong; 7, Sichuan; 8, Yunnan; 9, Anhui; 10, Jiangxi.

The leaves and tea products were ground and passed through a 0.45 mm sieve. There were three replicates for each sample.

The chemical reagents used here were of analytical grade.

Measurement of Fluoride Content. F concentrations in tea samples were determined according to the method described by Sha and Zheng (*17*). A 0.2 g portion of each sample was extracted in 10 mL of 1 N HCl at 100 °C for 1 h and then cooled to room temperature. To calibrate the standard curve, NaF solution was used as a standard solution. Ten milliliters of standard F solution or sample was added to 25 mL of freshly prepared total ionic strength adjusting buffer (3 M sodium acetate/0.75 M sodium citrate = 1:1), and then the volume was made up to 50 mL with distilled deionized water. The F content was measured with a fluoride ion-selective electrode.

Measurement of the Contents of the Quality Parameters. The content of total polyphenols in the samples was determined according to a spectrophotometric method with a dyeing solution of ferrous tartrate (*18*, *19*). The content of amino acids was determined according to a spectrophotometric method with ninhydrin dyeing (*18*, *19*).

RESULTS AND DISCUSSION

Although tea plants are known as F accumulators, information is lacking on the relationship of F level and the quality of tea products. The aim of this study was to investigate the variation in the F level with the maturity of tea shoots and whether any correlation exists between F level and the quality grades of the made teas.

Distribution of F in Different Parts of Tea Shoots: Fast Increase of F with the Growth of the Leaves. The fresh leaves were collected from 14 plantations in eight provinces, which are the main producing provinces of tea in China (**Figure 1**). Because the F content can be influenced by the soil conditions of the plantations and the varieties of the tea plants (*7*, *9*, *11*), quantitative differences exist among the F level of the leaves from different plantations. However, there was consistent coincidence that the mature leaves accumulated more F than young leaves, irrespective of the varieties and plantations (**Table 1**). These results are consistent with previous studies (*10*−*12*).

In the young leaves, which are the raw materials for processing green tea and black tea, the F level varied from 100 to 430 mg/kg, and most of them were <200 mg/kg. In the old leaves, which are usually not used for tea processing, F content ranged from 530 to 2350 mg/kg. In most of the old leaves, it was >1000 mg/kg, 3−15 times the levels found in young leaves.

Table 1. F Content (Milligrams per Kilogram)[a] of Fresh Leaves from Different Plantations

plantation	young leaves[b]	old leaves[c]
Wufeng, Hubei[d]	194 ± 6	1158 ± 133
Changsha, Hunan	100 ± 9	1591 ± 366
Anhua, Hunan	319 ± 51	1271 ± 154
Gao County, Sichuan	388 ± 55	1229 ± 120
Suzhou, Jiangsu	430 ± 29	1308 ± 227
Hangzhou, Zhejiang (1)	152 ± 32	2325 ± 290
Hangzhou, Zhejiang (2)	243 ± 65	2346 ± 302
Wuyi, Zhejiang	115 ± 34	1474 ± 218
Longyan, Fujian (1)	106 ± 22	1218 ± 184
Longyan, Fujian (2)	118 ± 13	888 ± 128
Fuding, Fujian	235 ± 81	1001 ± 112
Wuyishan, Fujian	153 ± 6	520 ± 21
Simao, Yunnan	120 ± 12	542 ± 61
Chaozhou, Guangdong	110 ± 20	534 ± 37

[a] Values are mean ± SD. [b] Leaves usually for green tea and black tea. [c] Leaves usually not for green tea or black tea, but some are for brick tea. [d] For locations of the provinces in China see **Figure 1**.

Table 2. F Content (Milligrams per Kilogram) in Young Shoots

plantation	bud and first leaf	second leaf	third leaf	fourth leaf	fifth leaf	sixth leaf
Hangzhou, Zhejiang (1)	30	83 (2.8)[a]	189 (2.3)	315 (1.7)	628 (2.0)	889 (1.4)
Hangzhou, Zhejiang (2)	73	146 (2.0)	300 (2.0)	521 (1.7)	826 (1.6)	991 (1.2)
Wuyi, Zhejiang	60	169 (2.8)	250 (1.5)	371 (1.5)	434 (1.1)	510 (1.2)
Longyan, Fujian (1)	26	73 (2.8)	100 (1.4)	161 (1.6)	222 (1.4)	308 (1.4)
Longyan, Fujian (2)	29	87 (3.0)	138 (1.6)	198 (1.4)	238 (1.2)	287 (1.2)
Fuding, Fujian	74	138 (1.9)	262 (1.9)	470 (1.8)	760 (1.6)	800 (1.1)

[a] Numbers in the parentheses are the increasing rate of F content in the two adjacent leaves.

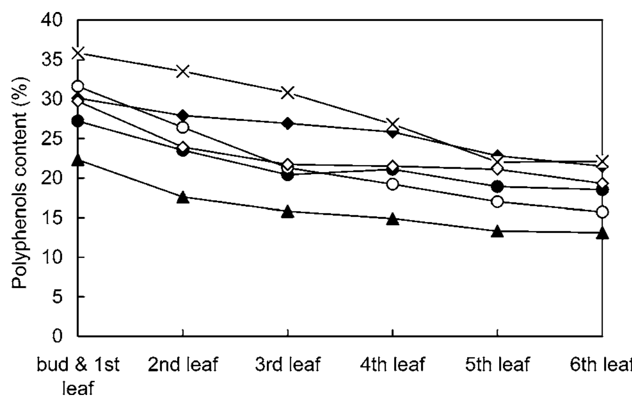

Figure 2. Total polyphenols content of the young shoots from the following plantations: (●) Hangzhou (1); (○) Hangzhou (2); (▲) Wuyi; (◆) Longyan (1); (◇) Longyan (2); (×) Fuding.

The tea shoots from southern regions contained less F than those from the north.

We also analyzed the F content of different leaf parts of young shoots collected from six tea plantations: Hangzhou (two plantations) and Wuyi in Zhejiang province and Fuding and Longyan (two plantations) in Fujian province, respectively (**Table 2**). A significant enhancement was observed in the F content due to maturity. The F content ranged from 30 to 75 mg/kg in the bud and first leaves and increased to the range of 300−1000 mg/kg in the sixth leaves. The biggest increase between adjacent leaves was 2.0−3.0 times, observed from the buds and first leaves to second leaves, and declined with shoot maturity to 1.0−1.4 times.

The study shows clearly that the F level is an indicator of the maturity. It suggests that the F level can be used to check

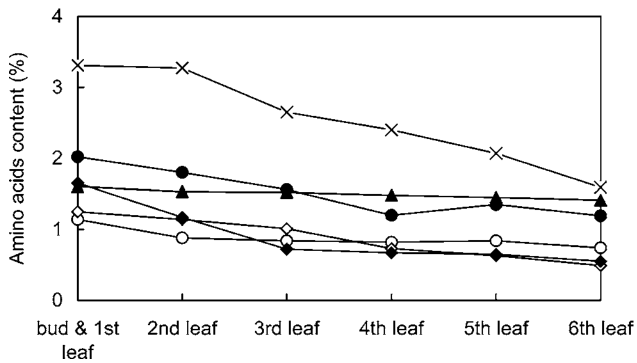

Figure 3. Amino acids content of the young shoots from the following plantations: (●) Hangzhou (1); (○) Hangzhou (2); (▲) Wuyi; (◆) Longyan (1); (◇) Longyan (2); (×) Fuding.

the fineness of plucking, which is a major factor that affects the quality of the made tea. Usually, the high-quality teas are made of tender shoots, and the quality deterioration with the coarse pluck is significant (*3*). Up to now, the maturity degree is checked by determination of the level of crude fiber, which is rather complicated and time-consuming. The above results suggested that the F level could play the same role as the crude fiber. Furthermore, the analysis of F is much simpler and needs a smaller amount of tea per sample.

Relationship between F Content and the Level of the Quality Parameters in Fresh Leaves: Negative Logarithm Relationship of F and Polyphenols. It has already been shown that the levels of most quality compounds, such as polyphenols, amino acids, caffeine, and volatile compounds, vary with shoot maturity (*1*, *3*, *20*, *21*). Here the trend is reversed from that of F.

The total polyphenols and amino acids in the young shoots from the above six plantations were analyzed; their contents were rich in buds and first leaves and decreased with maturity (**Figures 2** and **3**). These results are consistent with previous studies (*22*). The differences in the content of total polyphenols and amino acids from the buds and first leaves to the sixth leaves were ∼2 times less, whereas F achieved ∼10 times greater accumulation as shown in **Table 2**. The rise of the shoot maturity is accompanied by a marked increase in the F level and a minor decrease in polyphenols and amino acids.

The relationship between the total polyphenols content or amino acids and F content on the basis of different shoot maturity was determined (**Figures 4** and **5**). Similar patterns were found in all of the above six series of samples. As a noteworthy result, a significant negative logarithm relationship between F content and both total polyphenols content and amino acids content was obtained, and the correlation coefficients for total polyphenols contents were slightly high, which may imply some importance in the metabolism of polyphenols and F. It was demonstrated that the variation of F level can also reflect that of the quality parameters in fresh leaves. The polyphenols and their products contribute to the astringency, thickness, and color (*18*, *23*, *24*), whereas the amino acids contribute to the sweet and umami tastes (*25*). The variation of the polyphenols and amino acids gives rise to the variation in the quality of made tea directly, so it can be visualized that the F level would correlate with the quality of made tea.

F Content in Tea Products with Different Quality Grades: Negative Relationship. Table 3 demonstrates the F content of green tea, oolong tea, black tea, and jasmine tea products (made teas) from six provinces in China (**Figure 1**). These 12 brands of teas have four to seven quality grades, respectively. They were ranked by the professional tasters according to their appearance, aroma, taste, and infusion, etc., and used as standard samples for sensory evaluation. The low F content ranged from 29 to 252 mg/kg, indicating that all of the tea products were made from young shoots.

The difference of each type of made tea is interesting. Among these four types of made teas, the green tea and the black tea had the lowest F contents, ranging from 29 to 154 mg/kg and from 44 to 141 mg/kg, respectively. These indicated that the materials of these two teas had similar maturity degrees, in agreement with the fact that both of their plucking standards are usually one to three leaves and a bud, the so-called flush.

The oolong tea had a slightly higher F level than green tea and black tea, ranging from 76 to 176 mg/kg for super grade to

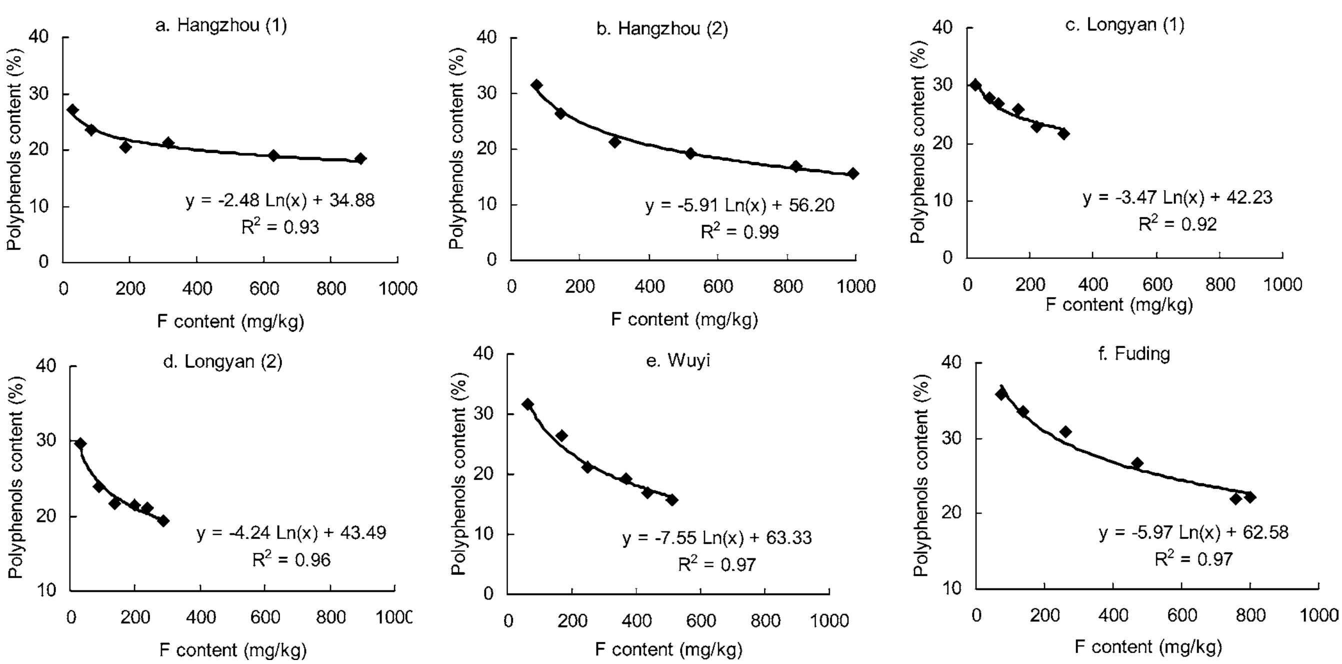

Figure 4. Relationship of polyphenols content and F content in young shoots. The fresh leaves were collected from six plantations (a–f) and divided into bud and first leaf, second leaf, third leaf, fourth leaf, fifth leaf, and sixth leaf, respectively.

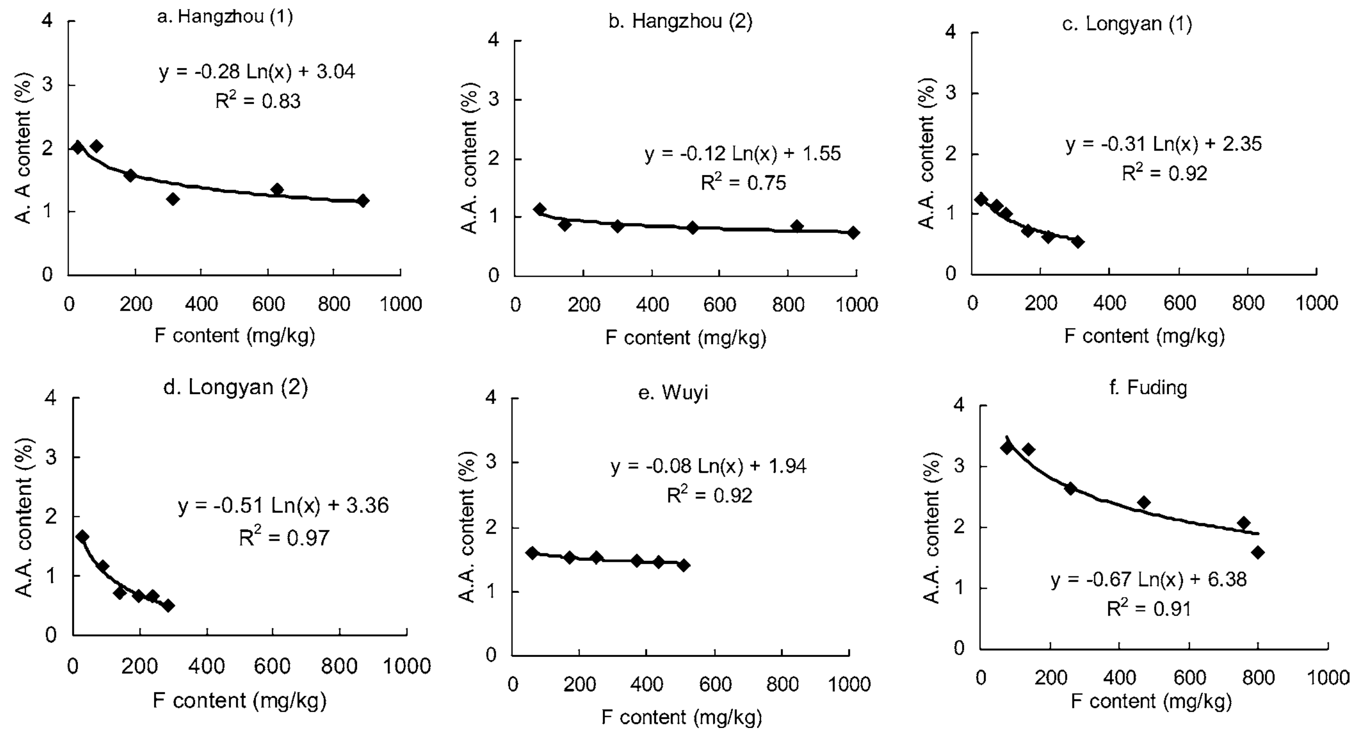

Figure 5. Relationship of amino acids (AA) content and F content in young shoots. The fresh leaves were collected from six plantations (a–f) and divided into bud and first leaf, second leaf, third leaf, fourth leaf, fifth leaf, and sixth leaf, respectively.

Table 3. F Content (Milligrams per Kilogram) in the Made Teas with Different Quality Grades

tea type	place	quality grade: super	1	2	3	4	5	6	linear coeff[a] (R)
green tea	Zhejiang[b]	29	37	36	43	49	61	74	0.95
	Zhejiang	31	44	45	56	54			0.93
	Zhejiang		109	124	120	134	134	154	0.93
	Jiangxi		64	64	71	73	74	82	0.95
	Fujian	58	63	62	78	79	74	125	0.81
black tea	Anhui		44	60	54	67	93		0.90
	Yunnan		61	76	81	84	97	87	0.89
	Zhejiang		61	68	89	88	121	141	0.96
jasmine tea	Hunan	76	85	93	84	124	173	198	0.91
	Zhejiang		146	153	158	192	206	252	0.95
oolong tea	Fujian	76	87	96	103				0.99
	Fujian	154	144	166	176				0.81

[a] Value of linear regression analyses between F contents and tea quality grades. Significant at $P \leq 0.01$. [b] For locations of the provinces in China see **Figure 1**.

grade 3 (there are usually only four grades for oolong tea). This is in line with the plucking standard of oolong tea, which is different from those for green tea or black tea. The flush for green tea and black tea cannot produce high-quality oolong tea because of its special processing. The material for oolong tea is the shoots of three to four leaves plucked after the banjhi (the bud at the stage of stopping growth) forms, when the leaves have been larger than the leaves of equal numbers of the shoots for green tea and black tea. That is why even the oolong teas of super grade and grade 1 have relatively high F levels.

The jasmine tea had the highest F level, 76−252 mg/kg, among the four types, which can be explained by the fact that jasmine tea is usually made from green tea of a somewhat lower quality grade; that is, the material is relatively mature. These results showed that the F level could reflect the plucking standard of the material.

It should be noted that the comparison of the tea products with different quality grades showed the higher the quality grade, the less the F content, and high linear coefficients were obtained. This can be well explained by the results above (high correlations of F level with the maturity of tea shoots and the level of quality parameters) and the fact that the difference of quality of the made tea is mainly caused by the maturity of the fresh leaves.

Although the F levels in different series of tea samples of different sources are quite different and there is not a universal relationship to calculate the quality grade, the linear coefficients for the individual series are quite high (**Table 3**). The results demonstrate that the F levels reflect not only the maturity degree of the fresh leaves but also the variation of the quality compounds whose levels changed with the shoot maturity and the quality of the made tea. These suggested that F could be regarded as a qualitatively important element in tea and that the F level could be useful for the quality estimation of tea products of definite sources. Furthermore, the analysis of F content is simple and needs little time, labor, and reagents compared to the analytical methods of other chemical parameters.

Quality grade is not a classification with any quantitative index but is decided by sensory evaluation. There is not a commonly applicable parameter as good as F found here to reflect the quality grade of tea. On the other hand, as the range of F content in teas from different producing areas is so wide, consumers can choose tea as a source of F or drink the tea of lower F content to avoid overconsumption without changing their custom.

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