Analysis of Minerals in Tea by an Inductively Coupled Plasma-Atomic Emission Spectrometry

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Introduction

Combution flames provide a simple mean for converting inorganic elements in solution into free atoms. Once the free atoms are formed, they may be detected and determined quantitatively at the trace level by atomic absorption, emission or fluoresence spectroscopic techniques.

Recently, a new emission spectroscopic technique, an inductively coupled plasma atomic emission spectrometry, has become available as a promising technique in detecting inorganic elements in inorganic and organic substances, with a high sensitivity and accuracy.^{1,2)}

The author has applied an inductively coupled plasma atomic emission spectrometry on the assay of minerals in tea and the liquor of tea and obtained satifactory results regarding its high sensitivity, accuracy and rapidness as a new assay technique.³⁾

Instrument and operation

This system is based on the observation of atomic emission spectra when samples in the form of an aerosol, a generated vapor or powder are injected into an inductively coupled plasma atomization and excitation source.

Referring to Fig. 1, a quartz tube approximately 2.0 cm in diameter is set inside a coil connected to a high-frequency generator operating in the 27.12 MHz at generator output levels of 1.6-2.5 kw. The high-frequency energy is fed, via the tuning coupling unit, to the coil, creating an intense magnetic field. A plasma is formed when argon gas is ionized as it passes through this magnetic field at the flow rate of 1.5 l/min. The plasma attains to a gas temperature ranging 7,000-9,000 °K in the region of maximum eddy current flow. To prevent overheating of the quartz cylinder, the argon coolant gas is flowed tangentially at the 10 l/min by the inside wall of the quartz cylinder.

The sample from the nebulizer, carried by argon at the 1 l/\min flow rate, is injected into the core of the plasma. The light from the plasma is diffracted by the spectro-meter, and the spectra lines of the elements to be determined are simultaneously sensed by the photomultipliers. Signals from the photomultipliers are measured by the read-out consols and the results are recorded on the recorder. The block diagram of the instrument is shown in Fig. 2.

The author used an inductively coupled plasma emission quantometer made by the Shimazu Seisakusho Ltd, which named it ICPQ-100 (Plate 1). This quantometer equips a direct reading 23-channel photomultipliers, and 23 elements are simultaneously determined.

A rapid, direct determination of main elements in tea

Range of concentrations of main elements in tea so far reported is summarized in Table 1.

The interelement interferences in the determination of multielements in actual samples by this method was already reported.⁴⁾ Especially, K, Na, Ca, and Mg showed high interferences on the spectrum intensities of coexisting elements.⁴⁾

The interferences of the major elements of tea, such as K, Ca, Mg, Mn and P, on other minor



Fig. 1. Configuration of plasma torch



Fig. 2. Block diagram of ICPQ-100

elements, such as Al, Fe, Zn, Cu, Ni and B, were surveyed at the concentration levels found in the 100 ml solution made from the ash of 1 g tea.⁵⁾

At these concentration levels, the interelement interferences by the major elements excepting K were negligible on each minor element, as shown in Table 2.

The most abundant element, K, exerted an

effect on the spectrum intensities of Al, Mn, Fe, Ni, B and Na. However, by adding the proportional amount of K found in the ash of 1 g tea into the standard solutions to be used for making the calibration line to determine the concentration of each element, the interference of K on Al, Mn, Fe, Ni, B and Na was neglected.

By the use of the matrix solutions in which



Plate 1. ICPQ-100

Element	Con	tent (pj	pm)
K	18000	_	27000
Ca	2000		6000
Mg	2000	-	6000
P	3000		8000
Al	200		1500
Mn	200		1200
Na	100		200
Fe	80	-	270
Zn	10		40
в	10	<u></u>	20
Ni	1	-	3

Table 1. Elemental contents in tea leaf

twelve elements (K, Na, Ca, Mg, Al, Mn, Fe, Zn, Cu, Ni, B and P) were dissolved at three concentration levels (high, middle and low) found in the ash of 1 g tea, as shown in Table 3, a study on the precision of the ICP technique has also been carried out and relative standard deviations of 1% for Ca, Mg, Na, Al, Mn, Fe, Cu, Zn and P and of about 4% for B have been obtained for the multielement analyzing procedure, as summarized in Table 4. Furthermore, in the range of concentration of each element shown in Table 3, the spectrum intensities of each element gave a straight line, respectively.

Table 2. In	fluences of	the major	elements on s	pectrum in	tensity of	other elements
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****						Ele	ements					
Major elements	к	Na	Ca	Mg	Al	Mn	Fe	Zn	Cu	Ni	в	P
K		I	N	N	I	I	I	N	N	I	I	N
Ca	N	N		N	N	N	N	N	N	N	I	ľ
Mg	N	N	N	-	N	N	N	N	N	N	I	N
Mn	N	N	N	N	N		N	N	N	N	N	ľ
P	N	N	N	N	N	N	N	N	N	N	N	_

I: Interference, N: Non-interference

Table 3. Standard solution used for assaying the elemental concentrations in 1 g of tea

Cone			10 ³ μ	g/100 m	l				µg/1	00 ml		
conc.	K	Ca	Mg	Al	\mathbf{P}	Mn	Na	Fe	Cu	Zn	Ni	в
S ₁	20	1	6	2	2.2	1.5	100	100	50	25	20	10
S,	20	3	1	3	4.6	0.5	300	300	100	50	5	5
S ₃	20	6	3	1	9.1	1	500	500	150	100	10	20

Table 4. Assay results of elemental concentrations by using the standard solution of Table 3

	Conc.+	S+2	CV+3	K+4
			(%)	
Na	300	3	1.03	17
Ca	3000	16	0.55	75
Mg	3000	15	0.51	74
Al	2000	6	0.29	43
P	4600	18	0.38	119
Mn	1000	5	0.45	20
Fe	300	1.3	0.43	6.5
Cu	100	0.6	0.56	2.6
Zn	50	0.1	0.24	1.6
Ni	10	1.1	1.10	3.2
в	10	0.4	3.72	0.4

+ : µg/100ml

+2: Standard deviation for concentration (µg)

+3: Coefficient of variation

+4 : Concentration for one division of intensity value (μg) (These values show the slope of each calculation line) The Ca, Al and P contents in tea were compared between the conventional techniques and the ICP technique.³⁾

For the determination of Ca content in food samples, the intereference suppressing reagentatomic absorption spectrometry is usually used.

In this case, it is neccesary to add the sufficient amount of Sr for depressing the interferences of P and Mg which are abundant in foods. However, the Ca content in tea could be determined directly from the HCl solution of the ash of tea without adding Sr by the ICP technique, as shown in Table 5.

The Al and P contents in tea are assayed by alminone photometry and vanadate-molybdate yellow photometry, respectively. The Al and P contents in tea determined by the ICP technique coincided very closely with the Al and P contents obtained from the conventional methods, as

1.ma/100 ml)

					(µ8/100 m)
		Certified		AA	S ⁺³
Sample			ICP ⁺²	S	r.
		value		10000	100000
Orchard leaves	Ca	20900 ± 300	20000	16100	188000
NBS-1571	P	2100 ± 100	2150		
T - (A)+ M	Ca		2550	600	2350
lea (A)⁺, May	Р		1650		
Tea(A)+, August	Ca		2500	600	2300
	Ca		2450	800	2400
Tea (B)+, May	Р		1700		
Tra (D) to August	Ca		3550	1400	3300
rea(b), August	Р		1200		

Table 5. Contents of Ca and P in orchard leaves and tea leaves

+ : (A) Tadanishiki, (B) Benihomare

+2 : ICP...Inductively coupled plasma-atomic emission spectrometry

+3 : AAS...Atomic absorption spectrometry



Fig. 3. Correlation between Al contents in tea determined by ICP technique and Alminone photometry



Fig. 4. Correlation between P contents in tea determined by ICP technique and Vanadate molybdate yellow photometry

shown in Figs. 3 and 4.

These results revealed that the ICP technique was very useful to determine the inorganic elements in tea and it was possible to determine simultaneously twelve main elements in a sample in 3–4 min.

Element	Max.	Min.	x	s
P	5550	3450	4608	529
Ca	3300	1430	2316	513
Mg	2350	1250	1693	258
Al	675	140	309	120
Mn	1080	190	609	230
Fe	260	80	123	32
Cu	24	7	12.1	2.9
Zn	252	38	73	39
Na	258	25	78	52
Ni	11.5	0.1	3.2	2.6
в	27	6	11.1	4.0

Table 6. Contents of some elements in Japanese green teas ($\mu g/g$, 31 samples)

Samples : Produced areas and numbers Kantō 8, Chūbu 5, Kyūshu 6, Shizuoka 6, Kinki 6

Max. : Maximun value, Min: Minimun value

 $\overline{X}\,$: Mean value, $\,$ s : Standard deviation

Table 7.	Concentrations of some elements in	ł.
	foreign black teas ($\mu g/g$, 15 sample	s

Element	Max.	Min.	x	s
P	3600	2400	2957	389
Ca	5600	2950	4163	805
Mg	2300	1500	1803	239
Al	900	330	671	161
Mn	1280	260	628	303
Fe	290	110	196	53
Cu	71	11	29.5	17.1
Zn	117	11	32.4	24.1
Na	214	4	131	54
Ni	24	10	17.3	4.5
в	26	10	17.8	4.9

Samples : Produced areas and numbers

Northeast India 3, South India 2,

South China 4, Sri Lanka 4, Kenya 2

The contents of mineral elements in Japanese green teas and foreign black teas were determined by the ICP technique as summarized in Tables 6 and 7.⁶

The contents of P, Ca, Al, Cu, Zn and Ni between Japanese teas and foreign teas showed significant differences. The contents of P and Zn were higher in Japanese teas and the contents of Ca, Al, Cu and Ni were higher in foreigh teas. The mineral contents in tea may have the geographic characteristics among tea producing areas, deriving from soil specificities or cultivation techniques (Table 8).

Element	Foreign black tea	Japanese green tea	(F)
Р	2957 ± 389	4608 ± 529	+
Ca	4163 ± 805	2316 ± 513	+
Al	671 ±161	309 ±120	+
Cu	29.5 ± 17.1	12.1 ± 2.9	++
Zn	32.4 ± 24.1	72.5 ± 39.4	+
Ni	17.3 ± 4.5	3.2 ± 2.6	+

Table 8. Comparison of elemental contents between Japanese green tea and foreign black tea $(\mu g/g)$

+ : Significant level, P < 5%

++ : Significant level, P < 1%

A convenient assay technique for elements in the liquor of tea⁷

Elemental concentrations in tea liquor were compared between two samples by using the ICP technique for the elements except K and a flame photometry for K. The one was prepared by the conventional preparation method, by which the liquor was concentrated, dried and laid to ash, and the ash was dissolved in the HCl solution before the assay. The other was not pretreated but assayed directly.

The standard solutions for assaying elemental concentrations in tea liquor were prepared as shown in Table 9.

The concentrations of Ca, Mg, Al, Mn, Zn, B, P and K in tea liquor showed no significant differences between the both preparations (Table

	fusion	concentrations (µg	s/100 ml)
Element	А	B+	C+
Ca	ł	500	1,000
Mg	tai	2,000	1,000
Al	IUC	1,000	500
Na	L C	250	500
Mn	N.	100	200
Fe	ut f 1	100	50
Zn	o sol	50	25
Cu	ΞĒ	10	20
Ni	H SS	10	20

Table 9. Standard solutions used for assaying

+ : B, C solutions are made by adding each element in A solution

40

3,000

10). These results showed that it was possible to determine directly elemental concentrations in tea liquor without any pretreatments.

Among minerals contained in tea, Fe, Cu and Ni were not detected in tea liquor. It seems that the most parts of those elements are in the form of insoluble complexes in tea and are hardly extracted by hot water.

Ca and Al showed low solubilities: 5%-7%and less than 20% of the total amounts were extracted in hot water, respectively.

On the other hand, about 90% of K in tea was extracted. The solubilities of other elements were in the range of 30-50% as shown in Table 11.

The hot water soluble minerals were dissolved up to about 90% of their total amounts into

Table 10. Comparison of elemental concentrations between A & B samp samples prepared from each of three teas
(µg/100 ml)

в

P

Element _	Tea	ı-1	Tea	-2	Tea-3		
	A*	B*	A	В	Á I	В	
Ca	170	175	160	160	300	300	
Mg	1,040	1,070	1,000	1,050	240	240	
Al	510	500	210	210	600	620	
Mn	140	140	215	240	180	180	
Zn	36	35	16	15	33	35	
B	9.5	10	7.8	8	5	5	
P	1,345	1,260	980	1,000	650	650	
K	28, 300	28,700	-	557 -5.5.5C	9,690	9, 930	

Statistical differences between A & B group by F-distribution test were not found on eight elements. A*: HCl solution of ash made from tea infusion

B*: Tea infusion

20

1,500

Table 11. Elemental concentrations in the infusions of Sen-cha and Kamairi-cha made from same tea cultivars plucked on same days

Ele- ment	Repe- tition ⁺	Yabukita-1 ⁺¹			Yabukita-2 ⁺¹			Kanayamidori ⁺¹		
		Sen-cha	Kamairi- cha	Ash of tea	Sen-cha	Kamairi- cha	Ash of tea	Sen-cha	Kamairi- cha	Ash of tea
Ca	1st	109	104	3, 180	101	101	2, 750	107	101	2, 480
	Sum	163	171	(5%)	155	155	(7%)	174	155	(7%)
	1st	576	626	1, 550	1,005	1,005	2, 130	898	871	2, 050
Mg	2nd Sum	82 658	147 773	(46%)	107 1,112	161 1, 166	(53%)	134 1, 032	127 998	(50%)
	1st	80	80	620	84	60	580	107	87	740
A1	2nd Sum	34 114	30 110	(18%)	20 104	20 80	(16%)	34 141	27 114	(17%)
	1st	225	228	870	288	214	870	255	241	800
Mn	2nd Sum	40 265	67 295	(34%)	40 328	40 254	(33%)	40 295	40 281	(36%)
Zn	1st	17	10	48	20	19	40	26	25	55
	2nd Sum	4 21	4 14	(36%)	2 22	2 21	(54%)	5 31	5 30	(56%)
	1st	2.3	2.0	12	4.0	3.4	16	4.0	3.4	17
В	2nd Sum	0.7 3.0	0.7 2.7	(24%)	1.3 5.3	0.7 4.1	(30%)	2.0 6.0	1.3 4.7	(31%)
	1st	503	764	3, 200	1,039	1,126	4, 500	831	1, 112	3, 700
Р	2nd Sum	94 597	188 952	(25%)	335 1, 374	201 1, 327	(30%)	147 978	174 1, 286	(35%)
	1st	13, 270	11, 790	17,600	12,900	12, 160	17, 700	12, 530	13, 460	16, 500
K	2nd Sum	2, 810 16, 080	3, 650 15, 410	(90%)	3, 150 16, 050	3, 350 15, 510	(90%)	3, 080 15, 610	2, 950 16, 410	(97%)
Fe		tr	ace	88	tra	ace	123	trace		177
Cu Na		trace		12 156	trace trace		13 136	trace trace		12 80

(μ g/g of tea, %: ratio of the concentration of each element in infusion per that in tea)

+ : Repetition of infusion by using the same tea (3g) in 200 ml boling water, two times. 1st, 1st infusion. 2nd, 2nd infusion. Sum, sum of the both infusions.

+1: Yabukita-1 was made in Kanaya. Yabukita -2 and Kanayamidori were made in Kumamoto.

tea liquorly twice extractions (Table 12).

From these results, it was shown that the ICP technique was a convenient assay technique of elemental concentrations in soft drinks, such as tea liquor.

Conclusion

It was revealed that an ICP technique was a powerful and convenient assay technique of elemental concentrations in foods and beverages

T21t	1st infusion			2nd infusion			3rd infusion		
Element	1	2	Average	1	2	Average	1	2	Average
Ca	175	150	163 (53%)	85	85	85	52	50	51 (21%)
Mg	610	535	548 (77)	120	145	133 (18)	35	35	35
Al	103	98	100 (71)	30	30	30 (21)	10	10	10 (8)
Mn	69	69	69 (80)	14	16	15 (18)	2	3	(2)
Zn	8.5	8.5	8.5 (83)	1.5	2	1.8	trace	trace	
В	4	3	3,5 (50)	1.5	1.9	1.7 (25)	1.9	1.5	1.7 (25)
Р	460	460	460 (77)	90	120	105 (18)	30	30	30 (5)
К	8,000	7, 500	7,750 (71)	2, 900	1,900	2,400 (22)	900	750	258 (7)

Table 12. Solubilities of elements in tea by step-wise infusion (µg/100 ml)

%: Ratio of concentrate in each step solution per total concentrate in three step solutions

from this experiment. Especially, this technique is not only highly sensitive and accurate technique, but it can determine simultaneously multielements in a short time. Furthermore, the operation of this instrument and the assay technique do not require any special skills.

From these facts, the author considers that the ICP technique may take an important position as the standard assay method for inorganic element concentrations in inorganic and organic materials in the near future.

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