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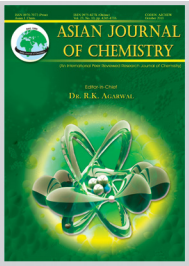

Simultaneous Determination of Ten Nutrient Elements in the Leaf of Gannan Navel Oranges from Southern Jiangxi by ICP-AES with Microwave Digestion

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A method for the simultaneous determination of Mn, Fe, Cu, Zn, K, Ca, Mg, P, B and S in leaf of navel oranges in southern Jiangxi by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after H_2O_2-HNO_3 microwave digestion was established. The method was verified by the determination of the reference materials (GBW10020). Values of detection limit of elements found were in the range of 0.15-76.8 μg L^{-1}. The proposed method was used in the analysis of navel orange leaves sample, giving values of RSD (n = 5) for the 10 elements in the range of 0.63-2.89 % and values of recovery in the range of 91.0-109.8 %. Leaf samples from 10 navel orange orchards were analyzed. The results show that the macronutrients K and P were higher than the corresponding suitable levels and the nutrients Ca, Zn, Cu and Mg were in low range. Therefore, the problems in fertilizer application in southern Jiangxi navel orange orchards were insufficient or excessive fertilizer application.

Key Words: Microwave digestion, ICP-AES, Leaf of navel orange, Nutrient element.

INTRODUCTION

As the unique soil conditions, Gannan Navel Orange produced from south of Jiangxi province of China, awarded the "Chinese famous fruit" honour, is very sweet and fragrant. Gannan navel orange, started to be grown from the 1970s, Gannan navel orange acreage has become the largest orange-producing main producing area of navel orange. However, most farmers empirically apply fertilizer in the production of Gannan navel orange, nutrition diagnosis of leaf and soil testing and formulated fertilization were little applied and emphasis on application of nitrogen, phosphorus, potassium and boron fertilizer, so resulted nutrient imbalance, yellow leaves, earlier recession of navel orange tree condition, which has become an important issue of the production of Gannan navel orange[1]. Leaf nutrient analysis is a mature nutritient diagnosis method for fruit trees, which has been widely used[2]. So detection and analysis of leaf nutrient elements is the basis of scientific application of fertilizers and reducing production costs of Gannan navel orange.

Leaf nutrient elements Mn, Fe, Cu, Zn, K, Ca, Mg are usually detected by AAS and P, B, S usually spectrophotometry after digestion or dry-ash by electric heating plate[3-6], experimental operation is very tedious, especially boron and sulfur detection methods demanding operating conditions, the workload is very large. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) has many advantages of low detection limit, good precision, linear range, multi-element determination and easy operation[7-9]. In this paper, 10 kinds of nutrient elements of navel orange leaves were simultaneously determined by ICP-AES method with microwave digestion for sample processing, the method is simple, fast, accurate and efficient, is a very practical method for the diagnosis of Gannan navel orange leaf nutrient conditions.

EXPERIMENTAL

Multiwave3000 microwave digestion instrument (Anton Paar Company, Austria); Synergy UVUltra-pure water instrument (Millipore Company, USA); Prodigy XP full spectrum inductively coupled plasma atomic emission spectrometry (ICP-AES) (Leeman company, USA); self-excited high-frequency generator, high-resolution echelle, resolution 0.009 nm (200 nm), vertical - horizontal double Observing System, CCD solid detector.

Reagents and standard solutions: Standard material of composition of citrus leaf (GBW10020) was bought from National Institute of Metrology; H_2O_2 (Guaranteed reagent), HNO_3 (guaranteed reagent); ultrapure water processed by Millipore instrument; glassware were all soaked by 10 % HNO_3 for 24 h.

Standard stock solution: standard solutions of manganese, iron, copper, zinc, potassium, calcium, magnesium and phos-

phorus were all bought from National Institute of Metrology, concentrations were all 1 mg mL^{-1}, the concentration of standard solution of sulfur (National Institute of Metrology) was 1 mg mL^{-1} (SO_4^{2-}), the concentration of standard solution of boron (bought from Steel Research Institute) was 100 mg mL^{-1}.

Mixed standard solution: The standard stock solutions were dubbed the required concentration of mixed standard solution with nitric acid (5 + 95). Standard solution groups were shown in Table-1.

TABLE-1
GROUPS OF STANDARD SOLUTIONS (μg mL^{-1})

Elements	1#	2#	3#	4#	5#	6#	7#	8#	9#	10#
Mn	0	0.1	1	10	–	–	–	–	–	–
Fe	0	0.5	5	50	–	–	–	–	–	–
Cu	0	0.1	1	10	–	–	–	–	–	–
Zn	0	0.1	1	10	–	–	–	–	–	–
K	0	–	–	–	1	10	100	–	–	–
Ca	0	–	–	–	3	30	300	–	–	–
Mg	0	–	–	–	0.5	5	50	–	–	–
P	0	–	–	–	–	–	–	0.5	5	50
B	0	–	–	–	–	–	–	0.1	1	10
$S(SO_4^{2-})$	0	–	–	–	–	–	–	1	10	100

Sample preparation: Freshly picked orange leaves were prepared referred to Zhuang's method[10]: Firstly washed in 0.1 % neutral detergent, take out and rinse with tap water as soon as possible; then washed with 0.2 % hydrochloric acid solution and washed with deionized water; leaves after washing were put on the filter paper to absorb moisture, then placed in drying oven at 105 ºC for 20 min to inactivate enzymes and dried at 65 ºC for 24 h, dried leaves were crushed with a stainless steel high-speed grinder, finally back into the sample bag.

Test method: Weigh accurately about 0.3 g the prepared samples in PTFE reactor, first pipette 3.5 mL nitric acid, then slowly add 2.5 mL hydrogen peroxide in the tank, standing a few minutes, digested in microwave digestion instrument. Digestion is completed, cooled and transferred to a 50 mL flask, constant volume with distilled water for detecting.

Instrument operating parameters: Incident power: 1.1 kW, Nebulizer pressure: 0.2 MPa, cooling air flow rate: 18 L min^{-1}, Auxiliary gas flow rate: 0.3 L min^{-1}, the enhanced amount of test solution: 1.4 mL min^{-1}, high purging and purging 1 h before the experiment, Mn, Fe, Cu, Zn, P, B and S were used horizontal observation, integration time 20 s; K, Ca, Mg were used vertical observation, integration time 5 s.

RESULTS AND DISCUSSION

Wavelength selection: Selecting several spectrum lines with less interference, high ratio of signal to noise when detecting each element, to scan the standard solution and sample solution to choose the spectrum line with less interference and high precision as the analysis wavelength (Table-2).

Impact test of acidity: Standard solutions were prepared by 2, 4, 6, 8 and 10 % nitrate solutions, respectively and detected according at the above conditions. The results showed that nitrate solutions have no effects when the concentrations are below 10 %. So samples added 3.5 mL when digested in nitric acid was can be directly tested on the machine after constant volume, which greatly reduced the sample handling time without catching acid.

Standard curve: The standard series solutions were detected at the selected conditions, drawing the work curve of each element by the instrument software automatically, linear correlation coefficients of all elements range from 0.99987-1.00000.

Detection limits: Measured blank solution 11 times repeatedly according to the above detecting conditions, take 3 times the standard deviation of the concentration value as the detection limit of each element, the results were showed in Table-2.

Precision of the method: The above test method was applied to the detection of ten kinds of elements (Mn, Fe, Cu, Zn, K, Ca, Mg, P, B and S) in standard material of citrus leaf (GBW10020), the results were showed in Table-3. Measured values are within the allowable range in the standard value, which indicate that the method is reliable.

TABLE-3
RESULTS OF MINERAL NUTRIENTS IN THE REFERENCE MATERIALS (n = 5)

Elements	Detected value (μg g^{-1})	Standards value (μg g^{-1})
Mn	29.2	30.5 ± 1.5
Fe	475.3	480 ± 30
Cu	6.8	6.6 ± 0.5
Zn	18.6	18 ± 2
K	7865	7700 ± 400
Ca	45677	42000 ± 4000
Mg	2396	2340 ± 70
P	1228	1250 ± 90
B	34	32 ± 3
S	4321	4100 ± 300

Recovery experiment: Accurately weighed about 0.3 g reference material samples of dried citrus leaves, adding the standard solution of Mn, Fe, Cu, Zn, P and B, detected contents of Mn, Fe, Cu, Zn, P and B according to test method. Because the contents of potassium, calcium, magnesium, sulfur in sample were high, they should be added after digestion, the 2 mL test solutions after digestion were added K, Ca, Mg and S reference solution volume to 10 mL, the recoveries of each element ranged from 91.0-109.8 % (Table-4).

TABLE-2
ANALYTICAL WAVELENGTHS AND DETECTION LIMITS OF ELEMENTS

Elements	Wavelength (nm)	Detection limits (μg L^{-1})	Elements	Wavelength (nm)	Detection limits (μg L^{-1})
Mn	259	0.15	Ca	315.887	8.76
Fe	259	1.40	Mg	285.213	2.81
Cu	324	0.51	P	213.618	13.35
Zn	213	0.76	B	249.772	0.45
K	766	52.60	$S(SO_4^{2-})$	182.034	76.80

TABLE-5
RESULTS OF NAVEL ORANGE LEAVES IN SOUTHERN JIANGXI (n = 5)

Elements	1#	2#	3#	4#	5#	6#	7#	8#	9#	10#
Mn (μg g^{-1})	14.96	25.64	18.19	21.80	27.25	22.72	28.21	34.71	21.12	46.18
Fe (μg g^{-1})	103.36	66.71	99.21	101.21	114.45	111.97	87.56	75.07	102.14	84.88
Cu (μg g^{-1})	12.88	5.77	3.55	5.15	5.05	7.18	4.11	2.50	5.83	13.62
Zn (μg g^{-1})	30.21	29.10	24.53	26.95	22.88	22.56	22.14	16.27	18.27	15.29
B (μg g^{-1})	69.28	73.20	94.48	113.51	96.07	94.92	74.79	129.05	88.99	95.18
K (%)	2.45	2.16	2.36	2.30	1.96	2.26	2.25	1.89	2.27	2.74
Ca (%)	3.15	2.82	3.08	3.08	3.18	2.88	3.14	1.86	3.00	2.22
Mg (%)	0.23	0.30	0.28	0.26	0.28	0.26	0.29	0.23	0.26	0.19
P (%)	0.17	0.19	0.18	0.17	0.17	0.18	0.17	0.19	0.20	0.18
S (%)	0.38	0.35	0.29	0.36	0.34	0.35	0.36	0.35	0.33	0.34

Note: Suitable range of refered to the US grading standards of sweet orange leaves[11], suitable range of Mn is 25-100 μg g^{-1}, suitable Fe range from 60-120 μg g^{-1}, Cu is 5-16 μg g^{-1}, Zn 25-100 μg g^{-1}, B 36-100 μg g^{-1}, K 1.2-1.7 %, Ca 3.0-4.9 %, Mg 0.30-0.49 %, P 0.12-0.16 % and S 0.20-0.39 %.

TABLE-4
RESULT OF RECOVERIES (n = 5)

Element	Background value (μg)	Standard dosage (μg)	Detected value (μg)	Average recovery (%)
Mn	9.948	10.00	20.48	105.3
Fe	161.9	200.0	353.1	95.6
Cu	2.317	2.000	4.137	91.0
Zn	6.337	10.00	15.44	91.0
K	107.2	100.0	207.8	100.6
Ca	622.5	500.0	1168	109.1
Mg	32.65	50.00	87.55	109.8
P	418.4	300.0	719.9	100.5

Measurement results: Ten samples collected from 10 different Ganzhou navel orange orchard, samples were prepared according to 1.3, determined by ICP-AES according to the above test methods under the selected experimental conditions, each sample was measured five times, relative standard deviations ranged from 0.63-2.89 % (Table-5). The results showed that three nutrition elements K, P were generally high, but the contents of Ca, Zn and Cu in Gannan navel orange leaves from some orchards were low, especially Mg. So it is concluded that insufficient application of fertilizer and excessive application of fertilizer are two issues of concern of Gannan navel orange orchard production.

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