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Elemental Analysis / ICPMS-2030

Simultaneous Determination of Heavy Metal and Mineral Contents in Fruit Juices using Inductively Coupled Plasma Mass Spectrometry

❑ Overview

In this work, fifteen heavy metals and mineral contents in fruit juices were simultaneously determined by inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion. The analysis results of different types of juices from local market were compared against the new US EPA and WHO regulation limits. The elemental contents were either well below the regulation limits or not detected. The ICP-MS method developed applying helium collision cell technology is fast, sensitive and stable. The method accuracy, repeatability and stability were verified.

❑ Introduction

The consumption of fruit juice beverages has been increasing over the years due to its higher nutritional contents compared to its counterparts. It is therefore important to determine and quantify the heavy metals present in these beverages for food safety [1]. Some heavy metals such as Cu, Fe, Mn and Mo are micronutrients. Though being essential for some physiological and biochemical functions of the human body, they may have potential to cause acute or chronic toxicities if their contents are too high. Other heavy metals like As, Cd, Pb and Tl are of the particular concern due to their high toxicity and harmful impact on human health.

The World Health Organization (WHO) and United States Environmental Protection Agency (EPA) have issued a list of regulatory guidelines of heavy elements in drinking water.[2,3] In this study, the concentrations of these elements were quantitated in four commercial fruit juices by ICP-MS method and compared against the WHO and US EPA guidelines values.

❑ Experimental

Sample preparation

A variety of packaged fruit juices including apple juice, yuzu juice, mango juice and guava juice were obtained from local market. These fruit samples were well-shaken prior to sample preparation to ensure homogeneity.

An aliquot of 10 mL of each juice sample was taken into a microwave digester vessel. 10 mL of concentrated nitric acid and 3 mL of hydrogen peroxide was added into each vessel. Closed-vessel microwave digestion was used to minimize the potential loss of volatile analytes. The digestion program is listed in Table 1. After digestion, the digestate was transferred into a polyethylene (PE) tube and topped up to 40 mL with ultrapure water. All digested sample solution was further diluted by 5 times before ICP-MS analysis, giving a total dilution factor (DF) of 20. For Apple and Yuzu juices, total digestion with clear digested sample solutions could be achieved. While for Mango and Guava juices, the digested sample solutions were left to stand for 15 minutes to allow the white residue to settle before further dilution.

Figure 1: ICPMS-2030

Analytical conditions

All analyses were carried out on Shimadzu ICPMS-2030 system equipped with a mini-torch for low Ar gas consumption. The instrument configuration and operation parameters are summarized in Table 2. Helium collision mode was applied to all the analytes to eliminate possible polyatomic interferences and to achieve lower detection limits.

Calibration curves

External calibration standards were prepared by mixing multi and single elements standards from Merck and Sigma-Aldrich. The calibration standards were prepared at 0.5, 1.0, 2.5, 5.0, 10.0, 20.0 and 40.0 µg/L, except for As, Cd, Pb and Tl which were calibrated up to 20.0 µg/L only. All calibration standards were prepared in 1% (v/v) nitric acid. Ho, Rh and Y were added as internal standards at a final concentration of 2.5 µg/L each using online internal standard (ISTD) addition kit.

Table 1: Microwave digestion program

Step	Time (min)
Ramp to 180°C	15
Hold at 180°C	10
Cool down	15

❑ Results and Discussion

Quantitative analysis of fruit juice samples

The analytical results of 15 elemental contents in different fruit juices were listed and compared to WHO and US EPA guidelines for drinking water in Table 3. Six elements (As, Ba, Cd, Cr, Cu and Pb) are regulated by both authorities. Fe, Mn and Tl are only regulated by EPA, while Ni is only regulated by WHO.

Barium, Chromium and Copper are regulated by WHO and US EPA but with different guideline values. All three elements were detected in the four fruit juice samples. The concentrations determined were much lower than the control limits.

Arsenic, especially in its inorganic form, is known to be one of the most toxic trace elements present in the environment. The As concentrations in the fruit juices measured were below the limit of 10 µg/L set by both WHO and US EPA. The results showed that the Apple juice contained highest As content of 1.49 µg/L, followed by mango juice and guava juice of 0.96 µg/L and 0.393 µg/L, respectively. As was not detected in yuzu juice.

Cadmium is a human carcinogen and it is toxic to kidneys, skeletal and respiratory system. According to the WHO and EPA guidelines, Cd concentration in drinking water must be lower than 3 and 5 µg/L, respectively. About 0.1 µg/L of Cd was detected in apple, mango and guava juices, which is well below the guideline values set by WHO and US EPA.

Lead is a well known toxic heavy metal which could affect body systems such as gastrointestinal and cardiovascular systems through cumulative exposure. Pb was not detected in the fruit juice samples, except for guava juice. The measured level was 2.45 µg/L, which was below the guideline values of 10 and 15 µg/L from WHO and EPA, respectively. The Pb detected in the guava juice may indicate that there could be possible contamination during the production or processing.

Table 2: Analytical conditions and ICP-MS parameters

Parameter	Setting
RF Power	1.20 kW
Sampling Depth	5.0 mm
Plasma Gas	Ar 8.0 L/min
Auxiliary Gas	Ar 1.10 L/min
Carrier Gas	Ar 0.70 L/min
Torch	Mini-Torch
Chamber	Cyclone Chamber
Chamber Temp.	5°C
No. of Scans	10 times
Cell Gas (He)	6.0 mL/min

Calibration linearity and detection limits

Calibrations of all targeted analytes show good linearities with r > 0.9995 as shown in Table 4. LODs and LOQs were calculated by 3 and 10 times the standard deviation of calibration blank.

Recovery and precision

Method recovery and precision were assessed by spiking 5 µg/L of each element into all four fruit juices before sample digestion. Recovery rates of 89-117% in apple juice, 88-105% in yuzu juice, 91-112% in mango juice and 89-110% in guava juice were obtained, indicating the robustness of the ICP-MS method to handle a variety of fruit juices shown in Table 5. Good analysis precisions were achieved with %RSD less than 2.5 for three replicates.

Analysis stability and reproducibility

Analysis stability of the method was assessed by analyzing a mixed standard of 5 µg/L continuously. The measurement was taken at every 30-minute interval and recovery was calculated. Figure 2 shows the stability of the 15 targeted elements over 5 hours, with all normalized recovery values within the range of 80% - 120%.

The internal standards (Ho, Rh and Y) intensity were plotted in Figure 3 to monitor the overall instrument drift normalized to t=0. Throughout the 5 hours, the intensities drift was less than 6%, demonstrating the excellent system stability.

Furthermore, day-to-day reproducibility of measured concentrations was checked using apple juice and mango juice samples on two consecutive days under the same analytical conditions. The percentage variation of the elements measured on different days were all within 20%, with majority of the analytes below 10%, indicating good reproducibility and robustness of the method.

Table 3: Quantitative results in fruit juices, MDLs and WHO and EPA guideline value (Unit in µg/L)

Element	Apple Juice Conc.	Yuzu Juice Conc.	Mango Juice Conc.	Guava Juice Conc.	MDL[b]	WHO (2017)	EPA (2018)
As	1.49	N.D.[a]	0.96	0.39	0.18	10	10
Ba	58.7	64.7	97.5	60.2	0.40	1300	2000
Cd	0.16	N.D.	0.11	0.11	0.05	3	5
Co	4.94	0.14	0.16	3.98	0.04	--	--
Cr	7.44	1.32	3.19	4.04	0.40	50	100
Cu	51.8	17.0	53.5	70.8	0.81	2000	1300
Fe	206	45.8	372	402	3.76	--	300[c]
Ga	26.9	28.0	44.2	26.3	0.58	--	--
Mn	343	15.0	120	130	0.20	--	50[c]
Mo	N.D.	N.D.	N.D.	1.19	0.11	--	--
Ni	8.42	2.46	7.8	14.7	0.97	70	NA
Pb	N.D.	N.D.	N.D.	2.45	0.09	10	15
Sr	49.1	94.9	155	154	0.12	--	--
Tl	0.44	N.D.	0.01	0.15	0.01	--	2
V	0.27	0.10	0.73	0.67	0.09	--	--

a - N.D.: not detected
b - MDL: method detection limits are calculated by LOQ*Dilution Factor (DF).
c - values highlighted in bold are secondary maximum contaminant levels (MCLs) which are non-enforceable as stated in EPA.

Table 4: Elements with analyzing mass, internal standards, cell gas mode, correlation coefficients (r), LODs and LOQs

Element	Mass	Internal Standard	Cell Gas	r	LOD (µg/L)	LOQ (µg/L)
As	75	Y	On	0.99997	0.003	0.009
Ba	138	Rh	On	0.99982	0.006	0.020
Cd	111	Rh	On	0.99998	0.001	0.003
Co	59	Y	On	0.99993	0.001	0.002
Cr	52	Y	On	0.99996	0.006	0.020
Cu	63	Y	On	0.99971	0.012	0.040
Fe	57	Y	On	0.99996	0.056	0.188
Ga	69	Y	On	0.99996	0.009	0.029
Mn	55	Y	On	0.99999	0.003	0.010
Mo	98	Rh	On	0.99994	0.002	0.005
Ni	60	Y	On	0.99983	0.015	0.048
Pb	206	Ho	On	0.99996	0.001	0.004
Sr	88	Y	On	0.99999	0.002	0.006
Tl	205	Ho	On	0.99963	0.000	0.001
V	51	Y	On	0.99997	0.001	0.004

Table 5: Spike recovery results of targeted elements in four fruit juices at 5 µg/L

Element	Apple Juice		Yuzu Juice		Mango Juice		Guava Juice	
	Spiked	Recovery	Spiked	Recovery	Spiked	Recovery	Spiked	Recovery
As	4.44	89%	4.52	90%	4.53	91%	4.51	90%
Ba	4.86	97%	4.94	99%	5.62	112%	5.00	100%
Cd	4.78	96%	4.82	96%	4.83	97%	4.66	93%
Co	4.79	96%	4.85	97%	4.90	98%	4.78	96%
Cr	4.84	97%	4.87	97%	4.95	99%	4.91	98%
Cu	4.24	85%	4.39	88%	4.58	92%	4.59	92%
Fe	5.80	116%	4.83	97%	5.00	100%	5.50	110%
Ga	4.72	94%	4.90	98%	5.15	103%	4.86	97%
Mn	5.83	117%	4.94	99%	4.80	96%	4.60	92%
Mo	5.24	105%	5.21	104%	5.26	105%	5.15	103%
Ni	4.66	93%	4.72	94%	4.62	92%	4.79	89%
Pb	4.89	98%	5.01	100%	5.10	102%	4.93	99%
Sr	5.08	102%	5.25	105%	5.07	101%	4.68	94%
Tl	5.00	100%	5.10	102%	5.16	103%	5.06	101%
V	4.93	99%	4.95	99%	4.98	100%	4.90	98%

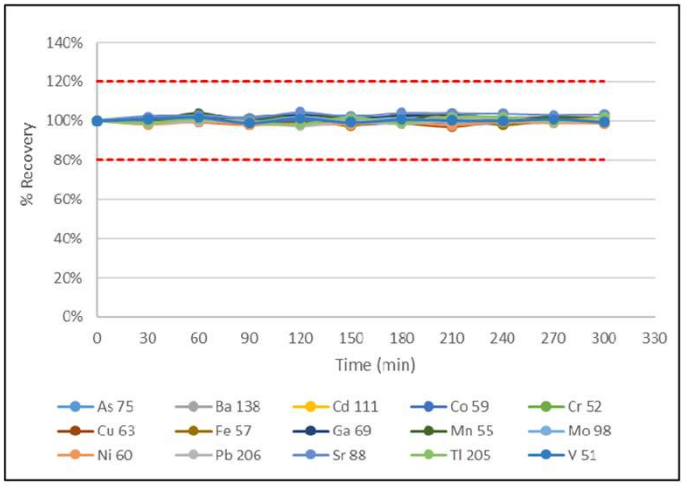

Figure 2: Normalized recovery tests over 5 hours (one analysis every 30 min)

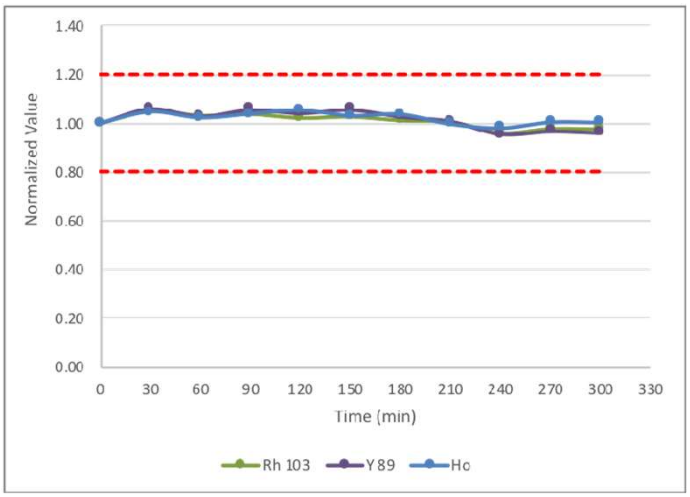

Figure 3: Normalized intensity of Internal standards over 5 hours

❑ Conclusion

A high throughput method was developed to simultaneously determine heavy metal and mineral contents in fruit juices by ICP-MS and microwave digester. The method was applied to analyze 15 elemental contents in four different types of fruit juices (apple, yuzu, mango and guava) from local market. The quantitated results were compared to the guideline values and the maximum contaminant levels (MCL) from WHO and US EPA regulations set for drinking water. The ICP-MS method established exhibited good calibration linearity and low method detection limits. The method recovery and precision were evaluated for all the targeted elements in the fruit juice samples.

Analysis stability and day-to-day reproducibility were also assessed. These results indicate that the ICP-MS method established is sensitive, accurate, stable and fast for determination of elemental contents in fruit juices. (15 elements in fruit juices samples.)

❑ References

1. A. Dehelean and D. A. Magdas, “Analysis of Some Romanian Fruit Juices by ICP-MS”, AIP Conference Proceedings 1565, 285 (2013)

2. World Health Organization (WHO). Guidelines for Drinking-water Quality, 4th ed., (2017)

3. US Environmental Protection Agency (EPA). National Primary Drinking Water Regulations, (2018)

❑ Acknowledgement

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