Rapid quantitative determination method of four heavy metals in strawberry

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Abstract: A rapid quantitative determination method of mercury, arsenic and arsenic, cadmium and chromium in strawberry was established. The sample to be tested was prepared into the solution to be tested, and the content of mercury, arsenic, cadmium and chromium were determined respectively on the machine. The results showed that the correlation coefficient of the standard curves of the four heavy metals was within 0.9961.000, and the detection limit was 0 mercury 0.028 g / kg, arsenic 0.062 g / kg, cadmium 0.14 g / kg, chromium 4.76 g / kg; the recovery was 80.2% 108.3% and 1.58% 26.34%; the test results of the standard samples were within the standard value. The method established in this experiment can determine the four heavy metals of mercury, arsenic, cadmium and chromium, etc. It has good linear correlation, low detection limit, good accuracy, high safety, simple operation, batch processing, and saves reagent consumables and detection time.

Keywords: courtyard strawberry; heavy metal; atomic fluorescence method; graphite furnace atomic absorption spectroscopy method; rapid detection; quantitative analysis

1. Introduction

Due to the industrial "three wastes", the natural environment itself and chemical fertilizer and pesticide residues, as well as the possible pollution of heavy metals in food processing, production, packaging and transportation, the problem of heavy metal pollution in agricultural products has become increasingly prominent [1]. Since 1994, the Ministry of Agriculture has issued and implemented the limit standards for heavy metals in food [2-4]. The update is more and faster, involving food categories more and more detailed, the country pays more and more attention to the content of heavy metals in food. Mercury, arsenic, cadmium, chromium, these four heavy metal elements are highly toxic and fatal harm to human body. However, because heavy metals need to accumulate for a period of time after entering, he human body to show their toxicity, it is often not easy to detect. Therefore, the risk monitoring of heavy metals should pay enough attention to it. This study combines the maximum limit of these four heavy metal elements in vegetables and fruits in GB2762-2012 National Standard of Pollutants in Food Safety and the detection limit of detection methods of these four heavy metal elements in the national standard [5-9], To establish a rapid quantitative determination method suitable for batch detection of these four heavy metal elements in strawberries during the strawberry planting season.

2. The Materials and Methods

2.1. Materials and reagents

Graphite pipe (general analysis of general purpose, Horizontal platform); Nitric acid deep superior grade pure); Thiourea deep analytical pure); Ascorbic acid deep analysis is pure); Potassium borohydride deep analysis is pure); Potassium hydroxide (analytically pure); Argon (Beijing Helium North Gas Industry, 99.9992%), Standard solution of mercury 1000 g/mL (Chinese Academy of Metrology, G B W08617); 100 g/mL (Chinese Academy of Metrology, GBW (E) 080117); 1000 Z g/mL (National Center for Analysis and Testing of Non-ferrous Metals and Electronic Materials, GSB 04-1721-2004); 1000 Z

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g/mL (National Center for Analysis and Testing of Non-ferrous Metals and Electronic Materials, GSB 04-1723-2004 (a)); G B W10048 (GSB-26) (National Standard Material, The Institute of Geophysical and Geochemical Exploration). All the glass instruments used were soaked in nitric acid (20%) for more than 24h, and finally washed and dried with water. Laboratory water is secondary distilled water.

Table 1: Working Conditions for Atomic Fluorescence Method Determination

Element	Total Lamp Current (mA)	Auxiliary Cathode Lamp	Photomultiplier Tube	Atomizer	Carrier Gas Flow (mL/min)	Shielding Gas Flow (mL/min)	Reductant	Current (mA)	Negative High Voltage (V)	Height (mm)
Total Hg	300	260	10	400	1000	1% KBH4	0.5% KOH	5% HNO3		
Total As	60	30	260	10	400	1000	2% KBH4			

Table 2: Working Conditions for Graphite Furnace Atomic Absorption Method Determination

Element	Wavelength (nm)	Lamp Current (mA)	Drying Temperature (°C)	Drying Time (s)	Ashing Temperature (°C)	Ashing Time (s)	Atomization Temperature (°C)	Atomization Time (s)	Purge Temperature (°C)	Purge Time (s)
Cd	228.8	0.4	120	10	350	10	1700	0	1800	2
Cr	357.9	0.4	100	10	500	10	2100			

2.2. Equipment and instruments

Atomic fluorescence photometer (Marine, AFS-9530); A3 atomic absorption spectrophotometer (GM, A3A F G-12); ultrasonic cleaning instrument (KQ-700 DE), digestion instrument (laser, E D54); electronic balance (Mettler, M S204S), ultrapure water meter (M IL L I-Q, clear-D24UV).

2.3. Test methods

1. Working conditions of the instrument. After sample digestion, the mercury and arsenic in strawberry of various heavy metal elements were determined by atomic fluorescence method. See Table 1. Cadmium and chromium in strawberries were determined by graphite furnace atomic absorption method, and the working conditions refer to Table 2.

2. Pre-sample processing. Test samples were strawberry samples extracted from each base in Changping, Beijing, stripping, homogenization, 5g (accurate to 0.001), 0.51h, 105°C digestion to colorless transparent or slightly yellow, open cover, acid to 12 mL, pure water to 50 mL, reagent blank, ultrasonic for 20min, mix to detect cadmium and chromium by 4 mL and 4 mL, and stand for 1h to detect mercury and arsenic.

3. Registration of the standard curve. The standard solution of mercury and arsenic is 5% nitric acid and 2% thiourea ascorbic acid as the solvent; the standard solution of cadmium and chromium is 2% nitric acid as the solvent to gradually dilute each reserve standard solution into the working solution.

4. Horizontal experiments. In the sample, four heavy metals were added at low, medium and high levels, and digested according to the method of sample pretreatment, acid driving, fixed volume, ultrasonic, computer detection, and repeated for 6 times. After removing the difference, the mean value is taken to reflect the results. When measurement, reagent blank was corrected to deduct background interference.

5. Data processing method. The metal element content is expressed as X and is calculated by formula (1).

$$X = (C — C_{。}) \ xV/WxF \tag{1}$$

Formula (1) is result (g / kg); blank concentration (g / L); direct reading concentration (g / L); fixed volume (mL); dilution ratio; W is sampling quantity, g. The detection limit DL is calculated according to formula (2).

$$DL = 3xSD/K \tag{2}$$

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In Equation (2), the standard deviation of the fluorescence value of the standard blank solution is SD, and the slope of the standard working curve is 1C.6. Detection of the standard samples. The national standard material GBW10048 (GSB-26) celery quality control sample was repeated 3 times

3. Results and the analysis

3.1. Drawing of the working curve

The working fluid of mercury and arsenic is diluted to the corresponding concentration by using the instrument. The working solution of cadmium and chromium is diluted to the corresponding concentration by using the linear equation by absorbance and fluorescence intensity respectively, as shown in Table 3. The correlation coefficient of the linear equations of the four heavy metal elements is between 0.9961, and the correlation linear is above 0.996, indicating that the correlation linear of these four heavy metal elements is good and meet the requirements of GB / T27404-2008.

Table 3: Linear Range and Correlation of Standard Curve

Element	Linear Equation	Correlation R	Linear Range of Standard Curve (ng/mL)
Total Hg	y = 688.143X + 7.267	0.9998	0.05, 0.1, 0.2, 0.4, 0.8, 1
Total As	y = 98.289X - 9.911	0.9998	0.5, 1, 2, 4, 8, 12, 20
Cd	y = 0.0932X - 0.0022	0.9967	0.5, 1, 2, 3, 4
Cr	y = 0.0106X - 0.0042	0.9995	5, 10, 20, 30, 40

3.2. Horizontal experiment

The four heavy metal elements were added at three horizontal concentrations, and each level was repeated six times. The spiked concentration and the measurement results are shown in Table 4. As can be seen from Table 4, the average recovery of the spike experiments at three levels is within the range of 80.2% 108.3%, and the coefficient of variation is within the range of 1.58% 26.34%. The recovery rate and coefficient of variation of the measured component content stipulated in GB / T27404- -2008 are shown in Table 4. As shown in Table 4, the recovery rate and coefficient of variation of the three horizontal tests tested by this method meet the requirements of GB / T27404- -2008.

Table 4: Recovery and Precision Test of Spiking at Three Levels (n=6)

Element Detected	Spiked Concentration (mg/kg)	Background Average Value (mg/kg)	Measured Average Value (mg/kg)	Average Recovery Rate (%)	Coefficient of Variation (%)	GB/T27404 — 2008[10] Requirements
Total Hg	1.5	0.000	1.360	90.7	20.53	60 to 120
	3.0	2.967	98.9	26.34		
	5.0	5.246	104.9	8.46		
Total As	10	6.800	16.855	100.5	7.44	60 to 120
	20	28.463	108.3	4.23		
	80	91.284	105.6	2.73		
Cd	1	0.235	1.110	87.5	20.85	60 to 120
	3	2.917	89.4	17.73		
	50	43.622	86.8	5.18	± 15	
Cr	10	15.682	22.495	68.1	1.58	60 to 120
	30	39.740	80.2	3.92		
	200	204.377	94.3	9.96	80 to 110	± 10

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Detection limit results are shown in Table 5. As can be seen from Table 5, the detection limits of mercury, arsenic, cadmium and chromium all meet the latest requirements of the national standards [6-9]. The detection limit of mercury, arsenic, cadmium and chromium is all higher than the national standard [6-9]The low limit value indicates that the detection limit of this method meets the national standard of quantitative detection and is higher than the national standard.

Table 5: Comparison of Method Detection Limits with Standard Detection Limits

Element Detected	Method Detection Limit (mg/kg)	Reference National Standard Detection Limit (mg/kg)
Total Hg	0.028	GB 5009.17— 2014[6] 3
Total As	0.062	GB 5009.11— 2014[7] 10
Cd	0.14	GB 5009.15— 2014[8] 1
Cr	4.76	GB 5009.123— 2014[9] 10

3.3. Determination of the standard samples

To further determine the accuracy of this method, the national standard material GBW10048 (GSB-26) celery quality control sample was repeated three times. The results of the testing are shown in Table 6. The results show that the average measurement values of celery GBW10048 (GSB-26) quality control samples are within the standard values.

Table 6: Determination Results of Celery GBW 10048 (GSB-26) Quality Control Sample (n=3)

Element Detected	Detected Content (mg/kg)	Measurement Values	Standard Values (mg/kg)
Total Hg	17.80	16.80	14.6 ± 2.4
	16.10		
	16.90		
Total As	325.50	321.50	390 ± 80
	319.80		
	322.27		
Cd	97.80	90.50	92 ± 6
	91.95		
	93.42		
Cr	1597.70	1399.50	1350 ± 220
	1471.65		
	1489.62		

4. Discuss

4.1. Digestion method

The traditional methods of dissolving agricultural products include microwave digestion, graphite digestion, electric heating plate digestion, dry ash and so on. Microwave digestion has a wide range of application, low blank value, complete digestion, high recovery rate and short time consumption, but microwave digestion has a high cost, high requirements for digestion tube, and the batch amount is small. Although the equipment cost of electric heating plate digestion is low, the treatment time is long, and there are disadvantages of uneven heating and personnel on duty. Dry ash is in high temperature burning, make the organic matter oxidation decomposition, the remaining inorganic matter for determination. This method has a long digestion cycle, more power consumption, more volatile loss, and low recovery rate. national standards [6-9]. In different heavy metal elements pretreatment methods are different, complicated operation, to determine the four kinds of heavy metals, reagents and consumables needed in

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large pretreatment with nitric acid and perchloric acid, hydrogen peroxide, hydrochloric acid, sulfuric acid mixed or take turn digestion, add acid, reagent blank composition complex, intense reaction, high blank value, low safety factor. The wet digestion method of nitric acid of graphite digestion instrument used in this test only needs one pretreatment method, which can detect four heavy metal elements of cadmium, chromium, mercury and arsenic simultaneously. It is easy to operate, consumes less of reagent consumables, and saves the cost. Graphite digestion instrument has the advantages of large batch processing and no need for experimpersonnel, high safety coefficient, and can be used in general laboratories. In this experiment, only nitric acid was used to nitsolve the sample, and the sample was pre-digested. It has a high safety factor, the sample blank composition is simple and the blank value is low.105C was used for digestion. Although it is reported that 120°c was the highest temperature of cadmium, lead, mercury and arsenic in vegetables, we used 105C for digestion due to the volatile nature of mercury.

4.2. Detection method

The traditional methods of measuring heavy metal elements include atomic fluorescence method, atomic absorption method, ICP-MS method and so on [14-15]. According to the national standard GB5009.17-2014 total mercury determination and GB5009.11-2014 total arsenic determination, the first method is atomic fluorescence spectral analysis. Although the first method of total arsenic determination is ICP-MS, the second method is used in this experiment to further save the cost. According to the national standard GB5009.15-2014 cadmium determination and GB5009.13-2003 chromium determination, the first method of cadmium and chromium.

5. Conclusion

In this experiment, only one pretreatment can meet the detection requirements of four heavy metal elements, the relevant linearity of the calibration curve, the precision and recovery of the three levels and the accuracy of the standard sample all meet the requirements of the national standard GB / T27404-2008, and the detection limit is lower than the national standard [6-9] medium limit value. Therefore, the standard curve of this method has strong linear correlation, low detection limit, good accuracy, simple operation, high safety, large batch volume, save reagent consumables and time, and can realize accurate and rapid quantitative detection of mercury, arsenic, cadmium and chromium in strawberry.

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