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Determination of Cadmium in Rice by Dispersive Liquid-Liquid Micro Extraction-Hydride Generation-Atomic Fluorescence Spectrometry

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A method of determining trace cadmium in rice by dispersive liquid-liquid micro extraction coupled with hydride generation atomic fluorescence spectrometry was established using dithizone as a chelating agent, carbon tetrachloride as a solvent and ethanol as a dispersing agent. The influences of pH of aqueous solution, dithizone concentration, ethanol volume and carbon tetrachloride volume, times of extraction and centrifugation and interferences on the determination were investigated. Under the optimum experimental conditions, a linear relationship between the fluorescence intensity and cadmium concentration range of 0.005-10 μg/L was observed. The method showed a detection limit of 0.0015 μg/L cadmium and relative standard deviation of 2.10 % when applied to sample determination. A recovery of 95.2-103 % was obtained when the method was submitted to rice analysis. This method was also validated by national certified standard rice materials GB10010 and GB10015, showing a good agreement with the certified values. The method, attributed to its simplicity, fastness, accuracy, sensitivity and environmental friendliness, showed a great potential in the cadmium determination in a real work.

Keywords: Determination, Cadmium, Rice, Dispersive liquid-liquid micro extraction.

INTRODUCTION

Cadmium, a non essential element in living thing[1] and one of detrimental heavy metal elements to organisms, once accumulated, is difficult to release from our body[2]. When the human intake of cadmium exceeds a permit level, a variety of disease symptoms, such as heart failure, arteriosclerosis, bone pain *etc.*, will develop[3,4].

There are many evidences of the heavy metals disposals in our environment that challenges our tolerance, such as Longjiang river cadmium pollution in 2012 and Hejiang river thallium pollution in 2013 happened in Guangxi province of China, devastating people in this area. The main pollution source of heavy metals to human is from water and food. Once water is polluted and irrigated to crops, the heavy metals will be taken in, specially, by the paddy rice.

Rice provides abundant starch, vitamins, proteins, oryzanol and other nutrients with the functionalities of invigorating the spleen and the stomach and nourishing blood and other internal organs. As a main diet for oriental people, about 62 % people worldwide rely on rice for survival. Thus, the amount of cadmium in rice plays a pivot role in human health. The United Nations Food Standards Committee authorized the permit level in rice no more than 0.4 mg/kg. However, the standard is further restricted to less than 0.2 mg/kg in both China and European Union[5,6], which evidences that the cadmium pollutant in rice is a global problem, indicating the significance of controlling the cadmium in rice.

Cadmium amount in food samples is relatively low. Its determination could be not possible ruined by the interferences from sample matrix. It is impossible to determine cadmium directly without separation and concentration[7-9].

Liquid-liquid extraction is a popular method in sample treatment, in which the analyte of interest is extracted into an organic solvent, then concentrated and separated. This method with the virtues of simple operation and low cost is widely used. However, a substantial volume of organic solvents are utilized in this conventional extraction, of them are some toxic or hazardous solvents which pollute our environment. For many years, the sample preparation has been driven its way toward green as the technologies develop, desiring less and less solvent, or even no solvent at all. Thus, single drop micro-extraction (SDME), cloud point extraction (CPE), room temperature ion liquid extraction (RTILE) and dispersive liquid-liquid microextraction (DLLME), *etc.* have been developed[10]. In dispersive liquid-liquid microextraction, micro liters of solvent and dispersant are introduced in the sample solution to create an emulsion, which increases the contact surface between the solvent and analyte and facilitates the extraction process[11]. After phase separation by centrifugation, the solvent is possible to be directly injected into liquid chromatography, gas chromatography, graphite furnace atomic absorption spectrometry and other instrumentation for detection[12,13]. This method has been successfully used in the separation and concentration of metal elements and organics in terms of high ratio of concentration, low consumption of solvent and fast operation, showing a great prosperity in this area.

On other hand, hydride generation atomic fluorescence spectrometry with its great tolerance in interferences, wide range of linearity, low cost instrumentation, *etc*. is widely in determining trace metals[14,15]. In coupled with dispersive liquid-liquid microextraction, the instrument is conducted in this area[16].

In this paper, cadmium in the sample solution was separated and concentrated by dispersive liquid-liquid microextraction, where dithizone worked as a chelating reagent, ethanol as a dispersant and carbon tetrachloride as a solvent, then, determined by hydride generation-atomic fluorescence spectrometry. The method was applied to determine the cadmium in the rice samples from the United States, Brazil, France, Laos, *etc*., showing the advantages of simplicity, fastness and high ratio of enrichment.

EXPERIMENTAL

Atomic fluorescence spectrometer AFS-2202E (Beijing Kechuang Haiguang Co., China) was used to obtain the fluorescence intensity of the target element. Cadmium hollow vacuum cathode lamp (General Research Institute for Nonferrous Metals, China) provided an optical resource to excite the element of interest. Electronic balance AL104 (Mettler-Toledo Instruments (Shanghai) Co. Ltd., China) was utilized to obtain an appropriate sample weight or other chemicals when necessary. Centrifuge was carried out to facilitate the liquid-liquid micro extraction.

Standard solution of cadmium(II): An appropriate work solution was prepared by gradual dilution from its stock solution (1,000 μg/mL, GSB G 62040-90, National Center of Standard Materials, China). KBH_4 solution (15 g/L):1.5 g KBH_4 was dissolved in 100 mL NaOH of 5 g/L and diluted to 1 L. Fleshly prepared when needed.

Dithizone solution: A suitable amount of purified dithizone was dissolved in ethanol. Carbon tetrachloride, nitric acid, perchloric acid, ammonia, anhydrous ethanol, hydrochloric acid were all analytical grades. Deionized water was used in all cases.

Instrumental parameters: The spectrometer was operated under following parameters for determining the cadmium in samples: 300 V negative voltage; 60 mA lamp current; 8 mm atomic height; 400 mL/min carrier gas flow rate; 1000 mL/min shield gas flow rate; 15s measuring time; 1s delay time; peak area measuring mode; intermittent flow operation mode.

Sample digestion: Sample of 1 g was accurately weighed in a 100 mL beaker, covered with watch glass and 12 mL nitric acid and perchloric acid mixture (v:v/5:1) was added, soaked for overnight. Next, the sample was slowly heated to no fume and was almost dry. After removed from the hot plate and cooled to room temperature, the sample solution was filtrated into a 50 mL volumetric flask, adjusted its pH to 8, diluted to mark and mixed thoroughly. A blank was simultaneously prepared in the same manner.

Analytical method: An appropriate standard solution or sample solution of 5 mL was taken into a 10 mL centrifuge tube with a stopper. Then, 1 mL dithizone solution of 0.01 mmol/L and 1 mL carbon tetrachloride of 50 μL in ethanol were added. The solution was centrifuged for 4 min at 3000 rpm after kept to react for 3 min. Next that, the upper aqueous layer was removed and the solvent layer were evaporated to dry. Finally, the sample was dissolved with 5 mL HCl of 1 % in which cadmium was determined by AFS.

RESULTS AND DISCUSSION

Effect of pH on solvent extraction: The pH of the sample solution, which influenced both the stability of the coordination compound formed between cadmium and dithizone and the extraction efficiency, played an important role in the dispersive liquid-liquid micro extraction. The effect of pH on the solvent extraction was examined in the range of 5-11. Fig. 1 showed that the fluorescence intensity incremented as pH increased. However, after pH 8, at which maximum was achieved, the intensity decremented.

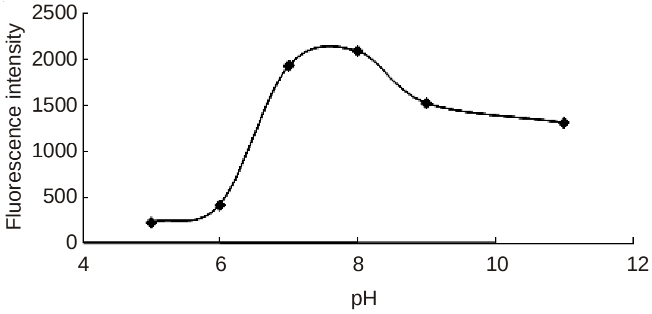

Fig. 1. Effect of pH on solvent extraction

Effect of dithizone concentration on solvent extraction: The formation of coordinated compound of cadmium and dithizone was guaranteed by an appropriate amount of chelating reagent, dithizone, which consequently affected the cadmium extraction efficiency. Thus, the investigation of the effect of dithizone concentration on the extraction was conducted in 0.002-0.12 mmol/L as exhibited in Fig. 2. It was found that as the dithizone concentration increased from 0.002 to 0.01 mmol/L, the fluorescence intensity increased accordingly. In contrast, the intensity decreased dramatically when more dithizones existed, indicating that more dithizones competed into solvent, reducing the coordinated compounds in the solvent.

Effect of carbon tetrachloride volume on solvent extraction: Carbon tetrachloride, a solvent widely used in cadmium extraction, was investigated for its influence of volume on the extraction. It was observed (Fig. 3) that between 10 and 50 μL, the intensity augmented with increase of the solvent volume. However, the intensity resulted in inversely

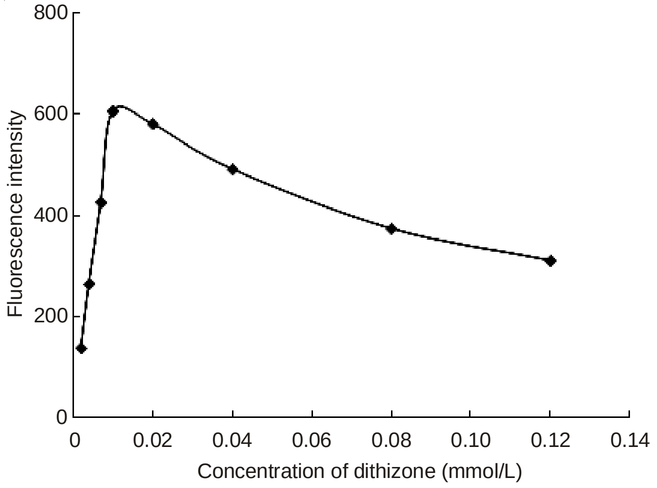

Fig. 2. Effect of dithizone concentration on the solvent extraction

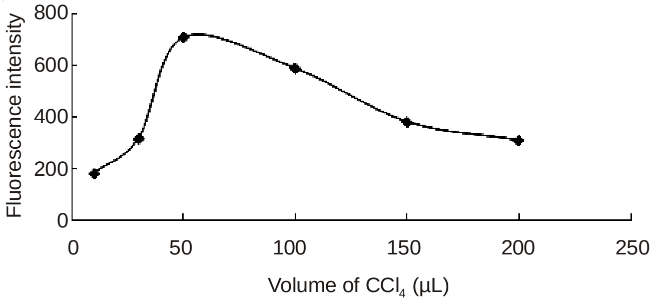

Fig. 3. Effect of solvent volume on the extraction

decrease after 50 µL, suggesting that the high volume of solvent benefited the formation of large sized droplets and deteriorated the formation of dispersive micro droplets, which dwindled the droplet number to enter solvent phase.

TABLE-1
ANALYTICAL RESULTS OF SAMPLES AND RECOVERIES (n = 5)

Sample#	Origins	Exp. values (µg/kg)	RSD (%)	Spiked (µg/kg)	Total (µg/kg)	Recovery (%)
1	Rice (San Francisco, USA)	28	2.6	20	47	97.9
				30	60	103
				40	66	97.1
2	Rice noodle (San Francisco, USA)	21	1.2	15	35	97.2
				20	40	95.2
				30	49	96.1
3	Pasta Roni (USA)	20	2.1	15	36	102
				20	41	102
				30	49	98
4	Hybrid rice (California, USA)	24	2.4	15	38	97.4
				20	46	104
				40	63	98.4
5	White glutinous Rice (Laos)	71	2.3	60	129	98.5
				70	138	97.8
				80	150	99.3
6	Glutinous Rice (Laos)	127	2.2	120	244	98.7
				130	260	101
				140	260	97.4
7	Brindle glutinous rice (Laos)	89	2.1	80	165	97.6
				90	180	100
				100	186	98.4
8	White glutinous rice (Laos)	79	2.1	70	151	101
				80	155	97.5
				100	178	99.4
9	Brown rice (Pampa, Brazil)	33	1.6	20	55	103
				30	64	101
				40	75	102
10	White rice (Pampa, Brazil)	31	2.2	20	53	103
				30	60	98.4
				40	73	102
11	Brown rice (USA)	21	1.2	15	35	97.2
				20	40	97.6
				30	49	96.1
12	Brown rice (Lafite, France)	46	2	40	83	96.5
				50	95	98.9
				60	102	96.2
13	White rice (Lafite, France)	63	2.2	50	110	97.3
				60	121	98.4
				70	129	96.9
14	GBW10010	86	0.7	/	/	/
15	GBW10015	171	1.1	/	/	/

Effect of dispersive agent on the extraction: Ethanol, due to its non-toxic, low cost and high extraction efficiency, was used as a dispersive agent. Its effect of volume on the extraction was studied in the series of 0.5, 0.8, 1.0, 1.2 and 1.5 mL. As it evidenced in Fig. 4, the intensity reached a maximum when 1 mL ethanol employed. Afterwards, the intensity experienced descending. It could be rationale that the carbon tetrachloride was difficult to disperse in the solution when ethanol volume was not large enough. On the other hand, the solubility of the coordinated compound, cadmium-dithizone, ascended in the aqueous phase when ethanol volume was too large, leading to low extraction efficiency.

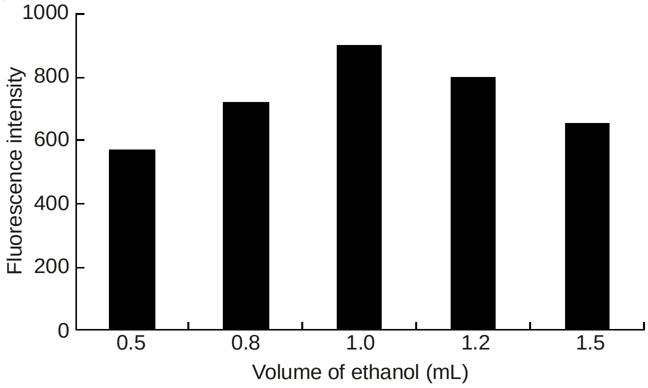

Fig. 4. Effect of ethanol volume on the extraction

Effect of times of extraction and centrifugation on the extraction: Extraction time was defined as the time from the formation of turbid solution to the centrifugation. It was evident that when the extraction was manipulated in 3 min, the intensity slightly increased and maintained almost constant after 3 min, showing that the dispersive liquid-liquid micro extraction occurred almost instantly.

When the speed of centrifugation was maintained 3000 rpm and the time was varied in 1, 2, 3, 4, 5, 8 and 10 min, the fluorescence intensity was constant after 4 min.

Interferences: The interference was oriented for these ions, potentially chelating with dithizone, in rice sample. Assuming detection error no greater than 5 %, it referred to no interference. Under optimum experimental conditions and cadmium concentration of 5 μg/L, 100 folds of Hg^{2+}, Cu^{2+}, 200 folds of Ba^{2+}, Ca^{2+} and 500 folds of Zn^{2+}, Mg^{2+}, Fe^{3+} did not interfere the determination. Na^+ and K^+ did not either.

Dynamic linearity and detection limit: Under optimum condition, the fluorescence intensity *vs* cadmium concentration showed a good linear relationship in the range of 0.005-10.0 μg/L with equation of $y = 230.719x-4.824$ and coefficient of 0.9938, where y was the intensity and x the concentration of cadmium. The detection limit was calculated 0.0015 μg/L based on 3 times of the standard deviation from a blank determined 11 times.

Sample analysis and method validation: The proposed method was validated with standard certified rice materials GBW10010 (87 ± 5 μg/kg) and GBW10015 (150 ± 25 μg/g) and applied to determine cadmium in rice sample of different origins with recoveries of 95.2-103 % (Table-1).

Conclusion

A novel method, based on dispersive liquid-liquid micro extraction in which dithizone as a chelating reagent, carbon tetrachloride as a solvent and ethanol as a dispersing agent, was established for the determination of cadmium in rice by hydride generation-atomic fluorescence spectrometry. In an optimum experimental condition, detection limit of 0.0015 μg/L and linear relationship of 0.005-10.0 μg /L were achieved. The relative standard deviation was 2.10 %. The method was validated with national standard certified rice materials, showing a good agreement with the certified values. The samples from a variety of origins were spiked and determined with recoveries of 95.2-103 %. The unique advantages of the method were environmental friendly (very small amount of solvent involved), high sensitivity, good accuracy, convenient operation, fast analytical speed, suggesting a great potential in determination of cadmium in rice.

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