Determination of the total chromium in vegetable, rice samples cultivated and marketed along Nhue River

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***Abstract*—** *The total chromium ions in vegetable and rice samples can be determined by spectrophotometric method using diphenylcarbazide reagent after their treatment. The treatment processes include: fresh sample treatment, digestion and oxidation of Cr(III) to Cr (VI). This oxidation was carried out very carefully using* $(NH)_2S_2O_8$ $AgNO_3$ *catalyst, NaCl then combining with* H_2O_2 *in alkaline media. The chromium contents in the root samples were higher than in the fresh stems samples (for spinach). In the same locations, if the chromium contents in the vegetable are high, the chromium contents in the rice samples are high too.*

Keywords*— *Rice sample, Vegetable sample, Chromium oxidation, Diphenylcarbazide.

I. INTRODUCTION

Rice and vegetables are daily used as food served as integral parts of a meal. So vegetables and rice constitute an important part of the human diet [1]. In vegetables and rice there are carbohydrates, proteins, as well as vitamins and minerals [1]. Vegetables can absorb metals from soil, water as well as from waste deposits on the parts of the vegetables exposed to the air from polluted environments [2]. As human activities are increasing, especially combining with the application of modern technologies and fertilizers, the pollution and contamination of the human food chain has become inevitable [3]. Besides, the number of elements, such as chromium (Cr), lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), copper (Cu)...in the high levels can be harmful to plants [4]. The heavy metals in the small concentrations from environment can be accumulated in foods (rice and vegetables). Heavy metals are one of a range of important types of contaminants that can be found on the surface and in the tissue of vegetables. For chromium, there are two common oxidation states present in environments such as Cr(III) and Cr(VI). The form of Cr(III) is considered to be the trace element essential for proper functioning of living organisms [5].The chromium state of Cr(VI) was reported to exert toxic effect on biological systems. Besides, Cr(VI) ions are the most mobile in environment of water and soil that are more available for living plants. Plants grow in the Cr(VI) contaminated environment often show an accumulation particularly in root tissue [5]. The mechanisms involved in the uptake and translocation of chromium in the plants is not understood at all. Because there is uncertainty about the ionic species present in different systems. There is however evidence that Cr(VI) is reduced to Cr(III) at the plant root surface and the irrespective of the chromium is retained in the roots [6,7]. This element, at the concentrations exceeding the physiological demand of vegetables, not only could cause toxic effect on them but also could enter food chains, get biomagnified and pose a potential threat to human health [8,9]. At present, the problem of contamination food and clean, safe food are of great interest [10]. In this article the presence of chromium in rice and vegetable samples were analyzed. All samples were collected along Nhue river. The water of Nhue river is used to watering vegetables and rice. The water from Nhue River was identified as a water resource contaminated by heavy metals [11]. The total chromium in the water spinach samples present in the roof and fresh stem part was analyzed. The presence of chromium in the rice and vegetable (water spinach) could allow an assessment of the safety levels of food (rice and vegetables) cultivated and marketed along Nhue River.

II. MATERIALS AND METHODS

2.1 Sample Collections

The rice and water spinach samples were collected from nine locations along Nhue River, Figure 1.

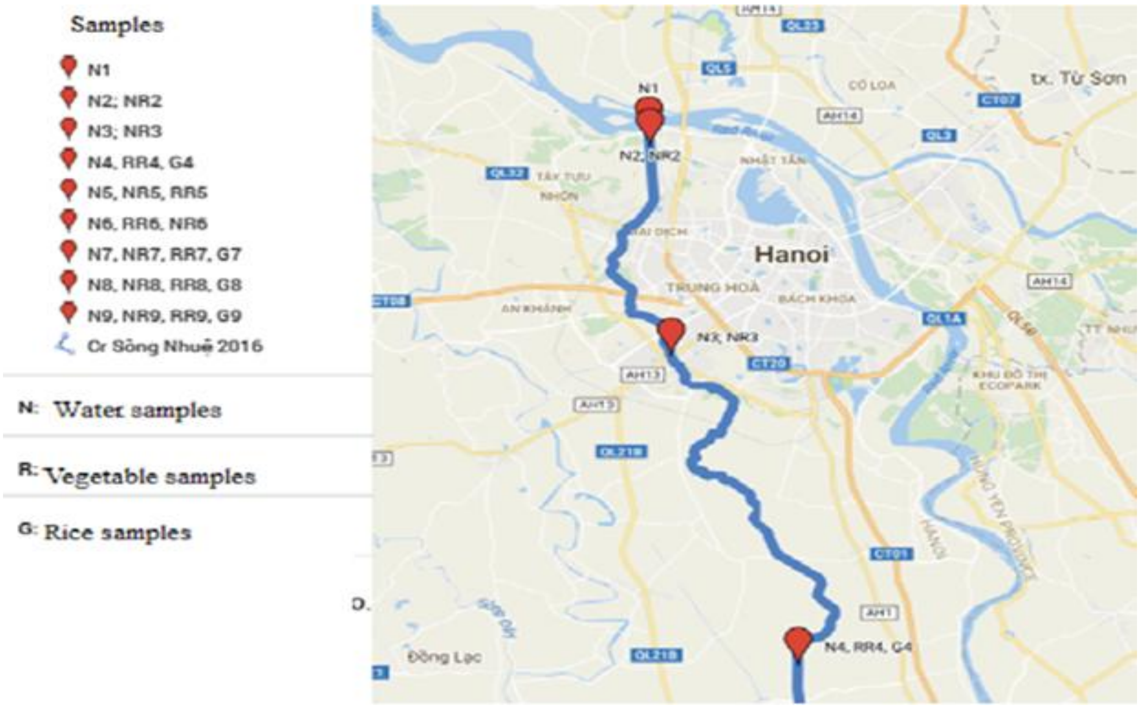

FIGURE 1. THE LOCATIONS OF COLLECTED SAMPLE ALONG NHUE RIVER

The total samples include rice spinach samples collected from different locations in 2015, 2016. Some vegetable samples were divided into fresh stem and root. All the vegetable samples (about 2,000 g) were washed with tap water to remove dust particles then finally with distilled water. All vegetable samples then were chopped into small pieces using a knife and kept air – dried condition before digestion.

2.2 Digestion of sample for total chromium determination

The rice and vegetable samples were weighed to determine the fresh weight and dried in a drying cabinet at 1000 C until the weigh being constant to determine their dry weight. The dry samples were crushed in a mortar to obtain uniform powder. The resulting powder digested by weighing 2.0 g (for the spinach samples), and 10.0 g (for rice samples) into an acid washed porcelain crucible, few drops of concentrated added, then placed in a muffle furnace for four hours at the range of 650 – 700^{o}C to ash. The crucibles with ash were removed from the furnace and cooled. Taken 5 mL (for vegetable sample) and 10 mL (for rice samples) 65 % concentrated HNO3 were added into crucibles, covered and heated on a steam bath to dissolve completely samples. The obtained solutions were used for to determine the total concentration in the samples of rice and vegetable.

2.3 Analysis of chromium in samples

The analysis of chromium in the samples was carried out using diphenylcarbazide reagent (DPC) based on measuring the absorbance of color compound being proportional to chromium at 541 nm. By our experimental study and combining with the work [12], a procedure of chromium determination was suggested as following (Figure 2.)

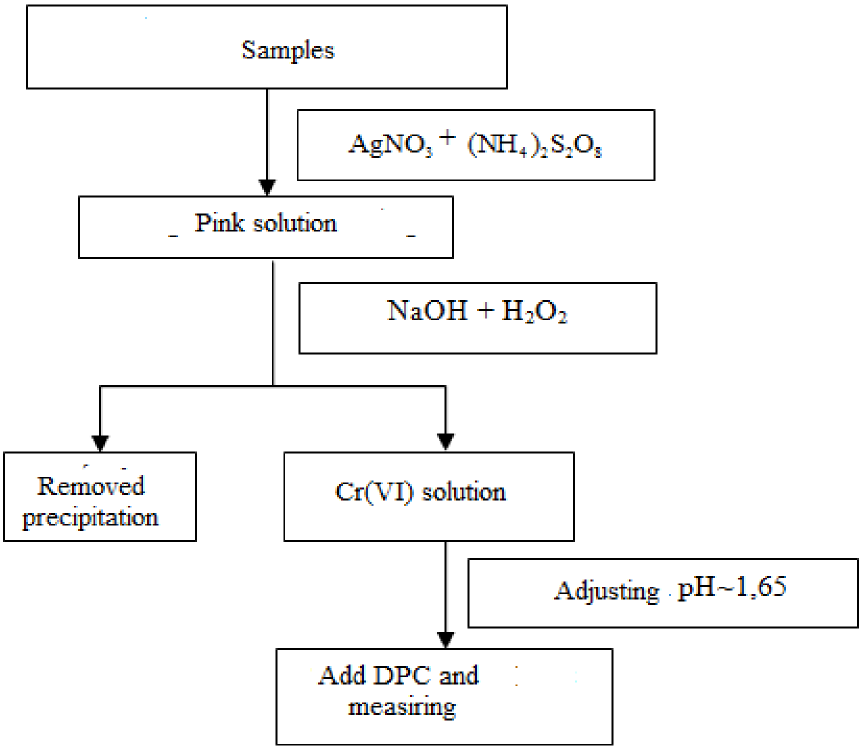

FIGURE 2. SCHEMA OF CHROMIUM ANALYSIS

As suggested in Figure 2, the oxidation of Cr(III) to Cr(VI) was carried out with $(NH_4)_2S_2O_8$, $AgNO_3$ catalyst combining with H_2O_2 in alkaline NaOH 8M. The obtained sample solutions in a glass beaker were heated on a steam bath, adding $AgNO_3$ solution, about 4 mL(for rice samples), 6 mL (for spinach samples) enough to remove Cl^- ions in precipitated AgCl. Adding 10 mL of $(NH_4)_2S_2O_8$ solution and the samples continued heating on the steam bath to oxidize Cr(III) to Cr(VI), pink color solution appeared. Adding 4 mL H_2O_2 (30 %) in the samples and then quickly add 10 mL NaOH (8M) waiting until a black precipitation appeared and remove this precipitation by filtration. The pH in the obtained samples was adjusted by HNO_3 (65%) about 0.1 mL to obtain pH = 1.65 before adding 0.8 mL DPC reagent. The obtained color solution with PDC was used for determination of chromium concentration in the samples by measurement of absorbance at the wave of 541 nm. This measurement was carried out using UV-Vis Biochrom S60, spectrophotometer, USA. The determination of chromium in the samples based on the standard conditions described in the work [13,14]. The sample without chromium should be used as a blank. The chemicals and solutions used for determination of chromium including $K_2Cr_2O_7$ (5 mg/L), HNO_3 (65%), NaOH (8M), $(NH_4)_2S_2O_8$(0.01M), $AgNO_3$(0.01M), NaCl (1%) and diphenylcarbazide, $(C_6H_6NHNH)_2CO$ (0.021M) were selected from Merck company.

III. RESULTS AND DISCUSSION

3.1 Standard plot used for determining chromium

By experiment at the standard conditions the standard plot was established and was presented by the equation as follows:

$$A = (0,8576 \pm 0,0411096)C_{Cr} + (0,02615 \pm 0,03420906) \quad (1)$$

After calculation with student- t distribution the standard equation has became:

$$A = (0,88 \pm 0,03)C_{Cr} \quad (2)$$

Basing on the standard equation the LOD (limit of detection) and LOQ (Limit of quantification) were determined as follows:

LOD = 0.010 mg/L; LOQ = 0.034 mg/L

So that, the obtained standard equation let's determine chromium concentrations in vegetable and rice samples.

3.2 Concentration of chromium in water spinach samples

3.2.1 Determination the ratio of dried samples per fresh samples

The weight of fresh and dried samples was presented in the Tables 1 and Table 2. The obtained results showed that the fresh stems of spinach contained more water than the roots. This is consistent with reality.

TABLE 1
RATIO (%) BETWEEN DRIED SAMPLES AND FRESH SAMPLES FOR FRESH STEMS

Samples	Fresh stem spinach samples m_{NR} (g)	Dried stem spinach samples m_{NR} (g)	Avarage weight $\overline{m}_{NR}$ (g)	$(\overline{m}_{NR} / m_{NR}).100$
1	460.00	39.80	39.81	86.54 %
2		39.82		
3		39.82		
4		39.79		
5		39.85		
6		39.76		
7		39.81		

TABLE 2
RATIO (%) BETWEEN DRIED SAMPLES AND FRESH SAMPLES FOR FRESH ROOT

Samples	Fresh root spinach samples m_{RR}, (g)	Dried root spinach samples m_{RR} (g)	Avarage weight $\overline{m_{RR}}$ (g)	$(\overline{m_{RR}} / m_{RR}).100$
1	770.00	73.28	73.26	95.14 %
2		73.24		
3		73.26		
4		73.25		
5		73.26		
6		73.27		

3.2.2 Determination of chromium in the spinach samples

The result of the total chromium concentration in the water spinach samples presented in Table 3 and in Figure 2.

TABLE 3
THE TOTAL CHROMIUM CONCENTRATIONS IN THE FRESH STEM

Nr.	Symbols	Absorbance (A) at (541nm)	C_{Cr} (mg/L)	C_{Cr} in 2 g of dried spinach stem samples (mg/2g)	C_{Cr} in fresh spinach sample (mg/kg)
1	NR_2	0.077	0.088	0.0022	0.095
2	NR_3	0.072	0.085	0.0022	0.095
3	NR_4	0.079	0.090	0.0022	0.097
4	NR_5	0.086	0,098	0.0024	0.106
5	NR_6	0.126	0.143	0.0036	0.155
6	NR_7	0.079	0.090	0.0022	0.097
7	NR_8	0.221	0.251	0.0063	0.272
8	NR_9	0.063	0.072	0.0018	0.077

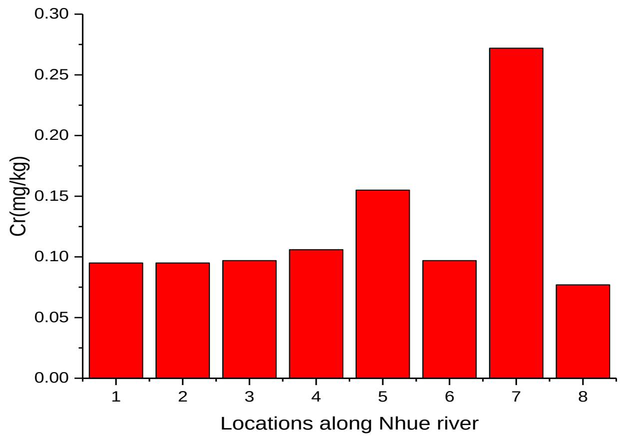

FIGURE 3. PLOT OF CHROMIUM CONTENT (FRESH STEM VEGETABLE) VERSUS LOCATIONS OF SAMPLES ALONG NHUE RIVER

The chromium contents in the fresh stem vegetable samples along Nhue river varied from the location 1 to the location 8. In the location 8 the chromium content was highest. This might due to the polluted environment around Nhue river. Here chromium content of the rice sample (G8 sample) is high too reaches to 1.9716 mg/kg. The experimental data of chromium contents in the fresh stem samples were smaller than in International/national standards for heavy metals in food [12].

TABLE 4
THE TOTAL CHROMIUM CONCENTRATIONS IN THE ROOT SAMPLES

Nr	Symbols	Absorbance (A) at (541nm)	C_{Cr} (mg/L)	C_{Cr} in 2 g of dried samples (mg/2g))	C_{Cr} in fresh sample (mg/kg)
1	RR_4	0.174	0.198	0.0049	0.235
2	RR_5	0.103	0.117	0.0029	0.139
3	RR_6	0.529	0.601	0.0150	0.715
4	RR_7	0.168	0.191	0.0048	0.227
5	RR_8	0.431	0.490	0.0122	0.582
6	RR_9	0.116	0.132	0.0033	0.157

The results of chromium in the water spinach samples showed that for the same spinach samples the chromium concentrations in the fresh stem and in the root were different see Table 5.

TABLE 5
THE CHROMIUM CONCENTRATIONS IN STEM AND ROOT IN THE SAME SAMPLES

Nr	Symbols	C_{Cr} /mg/kg in fresh spinach stem samples	C_{Cr} /mg/kg in fresh root samples
1	NR_4, RR_4	0.097	0.235
2	NR_5, RR_5	0.106	0.139
3	NR_6, RR_6	0.155	0.715
4	NR_7, RR_7	0.097	0.227
5	NR_8, RR_8	0.272	0.582
6	NR_9, RR_9	0.077	0.157

The experimental data in Table 4 showed that the chromium in the root samples was much higher than in the stem. These results are consistent with the works [8,9].

3.3 Concentration of chromium in rice samples

The chromium concentrations in the rice samples presented in Table 6 and Figure 3**.**

TABLE 6
CHROMIUM CONCENTRATION IN RICE SAMPLES

Nr.	Symbols	Absorbance (A) at (541nm)	C_{Cr} (mg/L)	C_{Cr} in 10 g of dried samples (mg/10g))	C_{Cr} in fresh rice sample (mg/kg)
1	G_4	0.204	0.237	0.0058	0.498
2	G_7	0.475	0.552	0.0135	1.160
3	G_8	0.789	0.917	0.0224	1.927
4	G_9	0.524	0.609	0.0149	1.280

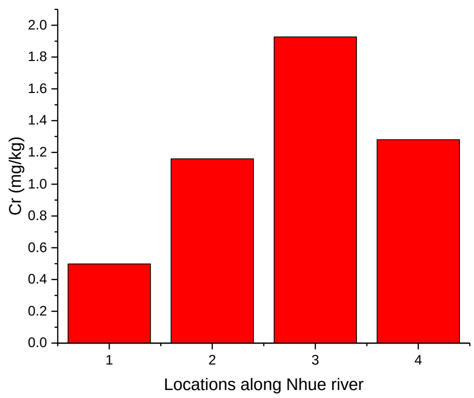

FIGURE 4. PLOT OF CHROMIUM CONTENTS OF RICE SAMPLES ALONG NHUE RIVER

The chromium contents in these samples are smaller than in the work [2] reported from Malaysia.

IV. CONCLUSION

Chromium ion from environment of water and soil can be absorbed by water spinach and rice plants. This is a problem needed to be carefully studied. A spectrophotometric measurement method used DPC reagent allowed determining chromium content in spinach samples (fresh stems and roots) and in rice samples collected from different locations along the Nhue River. Based on the standard curve, concentrations of chromium in the samples after treatment, oxidation Cr(III) to Cr (VI) by $(NH)_2$ S_2O_8 combining with H_2O_2 were determined. The chromium contents in the root samples were higher than in the fresh stems samples (for spinach). In the same locations, if the chromium contents in the vegetable are high, the chromium contents in the rice samples are high too. The experimental data showed the chromium levels in the rice and vegetables are within permissible standards for heavy metal in food as the WHO standard.

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