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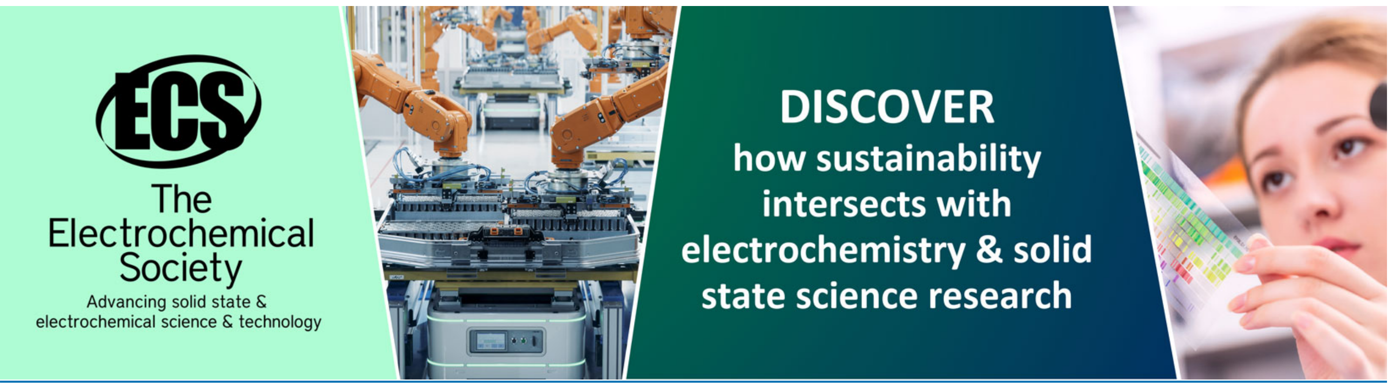

Identification of heavy metals on vegetables at the banks of Kaligarang river using neutron analysis activation method

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Abstract. This research aims to determine the type, concentration, and distribution of heavy metals in vegetables on the banks river Kaligarang using Neutron Analysis Activation (NAA) Method. The result is then compared to its predefined threshold. Vegetable samples included papaya leaf, cassava leaf, spinach, and water spinach. This research was conducted by taking a snippet of sediment and vegetation from 4 locations of Kaligarang river. These snippets are then prepared for further irradiated in the reactor for radioactive samples emiting γ-ray. The level of γ-ray energy determines the contained elements of sample that would be matched to Neutron Activation Table. The results showed that vegetablesat Kaligarang are containingCr-50,Co-59, Zn-64, Fe-58, and Mn-25, and well distributed at all research locations. Furthermore, the level of the detected metal elements is less than the predefined threshold.

1. Introduction

The growth acceleration of industrial development in a city in addition to causing positive impacts, can also cause various problems, especially the environment [1]. The activity of industries around a river [2-3] such as the Kaligarang River in Semarang City with heavy metal consuming causes the river pollution. There are several industries indicated to contribute heavy metal pollutants in the upper reaches of the river. Kaligarang river banks around the settlement found some vegetable crops are also consumed by the population. Plants that live around this river can be used as an indicator of heavy metal pollution, because plants live through absorbing water and other nutrients from sediment or soil around it, so that heavy metals in the river, possibly absorbed by plants [4-5]. Suparmingsih *et al.*showed that sediments in the Kaligarang River contained Co-59, Zn-64, Fe-58, Cr-50 and Mg-26 [6]. Research on the quality of Kaligarang River has been done with AANC method on sediment samples taken from Ungaran to Pleret, the result showsthat there are elements of heavy metal contamination in the form of Al-27; Si-28; Mn-55; Fe-56; Cu-63; Zn-64 and another research was doneon water samples taken from segments I to VII, with Atomic Absorption Spectrophotometer (AAS) method obtained by heavy metal contamination in the form of Cu, Zn, Cd, Pb, the colorimetric method obtained contamination of heavy metal Cr^{+6}, but the existence of this heavy metal has not exceeded the predefined threshold [7-11].

There are many methods to determine the heavy metal content of a material. Some research usesGFAAS (Analytik Jena AG/Konrad-Zuse-Straße) and ICP-OES [12]. Another method is the Neutron Activation Analysis Method (AAN) that has several advantages over other methods, which can observe the element type and the content although using relatively few samples (50-100mg) [13],

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does not damage the trailer [14], has a higher sensitivity until the nanogram (10^{-12} g) [15], can distinguish each isotope from the same footage, and can be used to determine the element content metallic elements in liquids, solids and gases [14]. An important advantage of the NAA method is the fact that the samples analyzed are not destroyed and can be used repeatedly [16].

This study aims to determine the type quantity of contaminants at vegetable samples living in the Banks Kaligarang River

2. Methods

2.1. Tools and materials
Samples of vegetables taken from the banks Kaligarang River. The tools used for collection are plastic clips, collisions, sieves, blenders, sample bottles, labels, digital balance sheets, paper, tissues, polyethylene vials, markers and cladding, while for irradiation and sampling using the Kartini reactor, set of γ spectrometers, set of computers, tweezers and Pb containers. The materials used in this study were 4 plant samples, 30 liters of nitrogen liquid, standard sources Am-241, Co-59, and Eu-152.

2.2. Sampling and sample preparation
Vegetable samples are taken from plants that live by the river, cleaned using local river water and put in plastic. The sample is dried to remove its water content [15]. Next pounded or blended and weighed as much as 0.05 grams, included in polyethylene vials. In plastic clips, coded and inserted in cladding.

2.3. Irradiation
How to activate the long-life element, the cladding containing the samples is included in the Lazy Susan irradiation facility and the irradiation time is set to 5 hours, while to activate the short-lived element, the cladding containing the sample is included in the Pneumatic irradiation facility and irradiated for 1 min.

2.4. Energy calibration
The energy calibration in this study used an Am-241 radioactive source that emitted energy-γ of 59.5 keV and Co-59 which emitted two γ-energies of 1173.2 keV and 1332.5 keV. Both of these radioactive sources are chosen for time efficiency, since the three emitted energies are sufficient to determine the relationship between the number of salur and energy. This radioactive source is enumerated for 3600 seconds, and the results of the enumeration are then poured in the graph of the relationship between the salur number (*x* axis) versus the gamma-ray power (*y* axis) with the following equation:

$$y = ax + b \tag{1}$$

2.5. Calibration of efficiency
The efficiency calibration aims to find the detection efficiency of the detector used, *i.e.* by comparing the count-rate received by the detector with emission rates from certain radiation sources. The efficiency calibration in this study was done by enumerating the radioactive source Eu-152 for 3600 seconds. The radioactive source Eu-152 is chosen because it emits a lot of energy, ranging from 121.78-1769.07 keV. In recording energy, replicating the resulting counters, *i.e.* cps, is needed for efficiency calibration. The energy obtained, matched with the Neutron Activation Table to obtain the value of yield or absolute intensity. The yield values are in cps and dpsthat are used to calculate the efficiency of each energy. The results of the efficiency calculations are presented in the graph of the relationship between gamma energy (x) versus efficiency (y), and formulated as follows:

$$y = ae^{-bx} \tag{2}$$

2.6. Enumeration
Prior to the enumeration, the sample was kept for ±5 minutes for the short half-life and 9 days for the long-life element, so that the element radioactivity can be properly detected by the detector. The sample enumeration used a set of γ-spectrometers for 5 minutes for a sample of half-life and 3 minutes for a short-lived sample. The enumeration results are stored in the Maestro program, so that they can be analyzed to be moved to the Genie program.

2.7. Qualitative analysis
Qualitative analysis aims to determine the types of elements contained in vegetables that grow on the banks Kaligarang River. The determination of this type of element is done by determining the peak of the gamma energy spectrum in the enumerated sample. The amount of gamma energy is matched with Neutron Activation Table, so it can be known what elements are contained in the sample.

2.8. Quantitative analysis
Quantitative analysis aims to determine the levels of heavy metals identified from qualitative analysis. The mass of heavy metal elements in the sample is obtainedby entering the parameters already known in the equation:

$$m_U = \frac{C\lambda B_A}{\varepsilon Y \phi\ \sigma\ N_A a(1-e^{-\lambda t_a})(e^{-\lambda t_d})(1-e^{-\lambda t_c})} \quad (3)$$

Heavy metal content is obtained from the heavy metal mass distribution that is identified by the sample mass:

$$K = \frac{m_U}{m_S} m_U \quad (4)$$

m_U is detected element mass and $m_S$is sample mass.

3. Result and Discussion
The results of qualitative analysis vegetable samples taken from the Banks of Kaligarang River presented in Table 1.

Table 1. Quantitative analysis of vegetable samples

Element	Papaya Leaf (μg/g)	Cassava Leaf (μg/g)	Spinach (μg/g)	Water Spinach (μg/g)
Cr-50	0.517$\pm$ 0.00144	0.751 $\pm$ 0.00030	0.771 $\pm$ 0.00011	0.561$\pm$ 0.00011
Co-59	0.568 $\pm$0.00158	0.518 $\pm$0.00137	0.268 $\pm$0.00110	0.178 $\pm$0.00110
Zn-64	10.37$\pm$0.15810	8.686$\pm$0.00213	6.668 $\pm$0.00198	5.988 $\pm$0.00198
Fe-58	1.469$\pm$0.00116	0.416 $\pm$0.00120	0.916 $\pm$0.00116	0.816 $\pm$0.00116
Mg-26	0.916 $\pm$0.00101	1.116 $\pm$0.00108	1.216 $\pm$0.00116	0.916 $\pm$0.00116

Table 1. shows some heavy metal elements detected on papaya leaf vegetable samples, cassava leaves, spinach vegetables, and water spinach, taken from Kaligarang River, also contained in Kaligarang River sediments [6]. This indicates that there is an element of sediment that transfers to the plant, for the survival of the plant required nutrients, minerals and water where the vegetables grow. Heavy metals accumulate in along time at soil and plants and may have a negative effect on plant physiological activity (*e.g.* photosynthesis, gas exchange, and nutrient absorption), determine plant growth decline, dry matter accumulation and crop yields [17-18].

The elements of chromium (Cr-50) contained in papaya leaves, cassava leaves, spinach, and water spinach, are still below the maximum permissible limit of 1.0 µg/g. Cr is one of high-toxic metals, heavy metal traces in non-toxic plants or animals of its small concentrations [19]. In addition, the level of poison power is not the same for all living things, depending on the ability of each individual to neutralize the toxic substances that enter the body. Cr content is caused because the vegetables are around the industrial area, Simongan. Chromium is usually integrated in textile dye molecules in significant quantities [20]. Cr sources also come from leather tanning factories, wheel renewal, Cr plating as well as petroleum burning, some of which this activity is in Simongan industrial area. Around the area there is a furniture industry, building stores and workshops that have a great opportunity to contribute Cr pollutants to the river body.

All vegetable samples in the banks of river contain Zn (zinc) elements. Zinc very important role in enzymatic activity as a co-factor and is present in various active groups of enzymes [21]. Zinc pollution also occurs in the Kaligarang river flow. Various studies have found zinc content with varying levels, in addition to other heavy metals [22]. The amount of detected Zn has not exceeded the established threshold of 120 μg/g [23]. Zinc is a constituent of several enzymes that play a role in chemical processes within cells, such as carbonic anhydrase, glutamate, lactate and alcohol dehydrogelas and alkaline phosphatase [24-25]. Excess metals can disrupt the metabolism of Fe in the body, while the shortage of this metal can lead to growth disorders, stunted maturity, skin lesions and depression immunity. Although Zn is a less toxic metal, if Zn consumption exceeds the prescribed limit it causes vomiting, diarrhea, fever, fatigue, anemia and reproductive disorders [26]. The location where this vegetable sample is the estuary of the Kaligarang River before it flows into the sea, and here there is also waste disposal directly to the river body so that the pollutants in this location is quite high.

Another metal detected in the vegetable sample is Fe (Iron). Iron is a component of haemoglobin that allows red blood cells to carry oxygen and deliver to body tissues. These metals include micro minerals essential to humans [27]. This mineral requirement is not the same depending on age and gender. Lack of this metal will cause fatigue and anemia. There for if the body of excess Fe will cause hemochromatosis and acute toxicity, cause vomiting, diarrhea and intestinal damage. Metal contamination of Fe is quite large, although still below the maximum limit allowed. Iron levels found in vegetables in this area, due to the growing area of vegetables, there are several metallic coatings and workshops that are likely to contribute Fe contamination in the river.

Magnesium (Mg) plays an important role for humans as electrolytes that regulate various biochemical reactions in the body[28]. The results of heavy metals research on Kaligarang River showed that there were Mg-26 elements in the vegetable samples. In this region there are various industrial activities that contribute Mg large enough to Kaligarang River. Place vegetables planted, located in the industrial area Simongan. In this region there are various factories that donate heavy metal pollutants to river bodies.

The content of Cobalt (Co) which is found is still far below the specified maximum limit of 25 μg/g.Cobalt is very important role in biological systems of living things bind as vitamin Cobalomin (B12). Co poisoning can occur when foods and drinks contain Co 150 ppm or more. Samples of vegetables taken in the industrial area Simongan. Simongan area is one of the industrial area so there are various factories that contribute heavy metal contamination to Kaligarang River. In addition, the amount of Co content, caused by Simongan close to the area of the Dewi Sartika which there are many workshops, waste sorting activities domestic waste coming from the settlement. The presence of Co in sediment and plant samples in Kaligarang River needs to be aware because Co is a moderate element that can cause health problems that can be recovered or not recovered for a relatively long period of time. The recommended daily intake for adults is 3 μg and only 50% are absorbed by the intestine [27]. This element is an essential element needed by plants to bind nitrogen in plant roots, and is an essential micro mineral for the body in the formation of vitamin B12, so this deficiency will lead to vitamin B12 deficiency. If excessive damage to the cardiovascular and lungs.

Education for people live around the river in consuming the healthy vegetables is needed to prevent bad effects that rises from consuming vegetables contained heavy metals in high degree. Need to grow the plants that are not to be consumed in the vicinity of the river. The type of plant that can be used to absorb heavy metals in river waters is eceng gondok (*Eichornia crassipes*). The surface of the root wall, stems and leaves have a very sensitive layer so that at an extreme depth of up to 8 meters below the surface of the water is still able to absorb sunlight and substances that dissolve below the water surface [29]. Water hyacinth with an area of 75% of the water surface area is able to absorb heavy metals optimally [30]. In addition to absorbing heavy metals in river waters, eceng gondok can also be used for various handicrafts that are economical. Sengon can also be used as a heavy metal absorber other than water hyacinth.

4. Conclusion

The heavy metals detected in the vegetable samples taken from the banks of Kaligarang River consist of Co-59 Zn-64, Fe-58, Cr-50, and Mg-26. The levels of the detected metal elements are less than the predefined threshold.

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