DETERMINATION OF PLATINUM GROUP ELEMENTS (PGE) IN SOIL AND GRASS USING ICP-MS IN UKM ENGINEERING LAKE

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Abstract.
Three elements in platinum group elements (PGE) which are platinum (Pt), palladium (Pd) and rhodium (Rh) are widely used in vehicle exhaust as catalyst in changing material and toxic gases such as CO, HC and NOx. However, the release of vehicle exhaust emission has increased the content of platinum group elements in the environment including dust, soil, water and grasses and sediments. The research aimed to determine the PGE content in grass and soil and to determine the concentration of Pt, Pd and Rh metals obtained in samples. The research was done at 4 station at UKM Engineering Lake, Malaysia. Analysis was done using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Result of the research showed that Rh metal was present at grass and soil sample. The Rh metal concentration in grass sample is between 1. 770 µg/g to 15.225 µg/g and in soil sample is between 2.347 µg/g to 9.579 µg/g. Pt and Pd were not detected in all samples and all stations. There are 80 other elements detected in the analysis. However, only four elements were taken into consideration which were Cu, Zn, Ni and Pb Since these elements were originated from vehicles activities. Their presence showed that Rh metal detected was from catalyzed changer in vehicles.

Keywords: PGE, Grass, Soil, ICP-MS, Lake

Introduction

Platinum group elements (PGE), particularly platinum (Pt), palladium (Pd) and rhodium (Rh) is used in catalytic converters in vehicle exhaust materials or toxic gases such as nitrogen oxides (NOx), unburned hydrogen (HC) and carbon monoxide (CO) that comes out to less-toxic substances. With the use of platinum group elements (PGE) in the device is expected to change this dangerous compound to compound that is more environmentally friendly as CO_2, N_2 and water. But it has caused much content platinum group elements in the environment such as dust, soil, water and sediments. Some of the platinum group metals can pollute the environment as a result of the absorption of this element in the plant, water and soil resources (Moldovan et al., 2001).

Contamination of platinum group initially occur in airborne particulate matter, dust, roadside soil, sludge and water. Platinum element is spread differently to the environment depends on the elements of the premier leak in the exhaust system, it also depends on the density of traffic and vehicle driving conditions (especially when starting, stopping vehicles and during acceleration). Age filter system also plays a role in the spread of this element to the external conditions (Dudding 2000).

This is the level of metal contamination remained below the level of concern, but it can be increased due to the popularity of the use of catalytic converters in developed countries. Therefore, it should be observed for the release of the platinum group metal elements so that they do not exceed a level and gave rise to many problems in the future, particularly in health.

Platinum group elements (PGE) is a difficult element found in the earth's crust. Since the use of catalytic converters in vehicles it has been found that platinum group elements released into the environment. Contamination of the platinum group elements initially occur through dust, soil, water, sediment, vegetation and eventually reaches a human. After platinum group elements released by the exhaust of vehicles equal to the dust, it will fall to the ground, the plant or are dispersed by wind, water and rain. Allowing platinum group elements (PGE) are also available around the lake have been studied UKM Engineering Lake. Therefore, this study was conducted on the grass and soil in the vicinity of the lake to examine the contents of platinum group elements in each sample and to determine the concentration of Pt, Pd and Rh metals obtained in samples.

Theoretical Framework

Platinum Group Elements (PGE)

In the periodic table there is a group of elements referred to as the platinum group elements (PGE). It is located in the eighth, nine and ten, on the fifth and sixth periods. It consists of 6 elements of platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os), all of which are difficult element is found and usually occurs naturally (The National Research Council 1977).

Platinum occurs naturally in the environment, particularly platinum ores and alloys. Platinum group elements, particularly platinum, palladium, and rhodium, are widely used in vehicle exhaust as a catalyst for change materials or toxic gases such as nitrogen oxides, unburned hydrogen and carbon monoxide that comes out to less-toxic substances. Some of the platinum group metals can pollute the environment as a result of the absorption of this element in the plant, water and soil resources (Moldovan et al., 2001). When erosion occurs on the outer layer of the metal, can cause metal platinum (Pt), palladium (Pd) and rhodium (Rh) is released into the environment. Erosion often occurs when shutting down and starting the vehicle (Neil 2004).

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Table 1. Abundance of Platinum Group Elements

Metals	concentration in the earth's crust, ppm
Palladium	0.01
Platinum	0.005
Rhodium	0.001
Iridium	0.001
Ruthenium	0.001
Osmonium	0.001

Source: Mason, 1958

Platinum group elements can now be found in industrial environments and objects environments, especially in road and tunnel dust, soil and vegetation near the road. In the industrial district, found the highest platinum group elements in river sediments. This may be caused by organic substances such as humic and fulvic acids that bind platinum and may be helped by the right pH and redox conditions on the probability of the aquatic environment. On land, the movement of platinum depends on pH, redox probability, the concentration of chloride in the groundwater and how the formation of platinum on primary rock (WHO 1991).

Catalytic Converter

The catalytic converter is a device designed to reduce the level of pollution, resulting from the release of contaminants from the exhaust vehicle. Vehicle exhaust release a lot of harmful gases into the environment as kabon monoxide, nitrogen oxides and unburned hydrocarbons. It can cause acid rain, smog or fog thick and respiratory disorders.

Catalytic converter can convert carbon monoxide, nitrogen oxides and unburned hydrocarbons into less toxic compounds, such as carbon dioxide, nitrogen and water (Barefoot, 1997; Brains 2001). These tools usually contain 0.10% to 0.15% (w / w) Pt, Pd and Rh to perform the conversion process contaminants (Ely et al., 2001).

Beginning in the 1970s, the United States has introduced a catalytic converter (Ely et al., 2001), followed by Germany in 1980 (Lesniewska et al., 2004). After the 1980s, Europe began to introduce catalytic converters and fully utilized in 1993 in the European Union (Jarvis et al., 2001).

Most catalytic converters are placed at the bottom of the front passenger seat of a vehicle, this allows the catalytic converter to function optimally. This is due to a catalytic converter works by engine temperature. When the cold temperatures, which new vehicle is turned on, a catalytic converter hardly do anything on gas emissions from vehicle engines. Catalytic converter will be functioning optimally at temperatures hot engine. But when the engine temperature is too hot, it can cause the catalyst in a catalytic converter tool is damaged and thus can not function properly (Nice 2004).
Use of catalytic converters have successfully reduced harmful gas up to 90% (Barefoot 1997). Although the use

of catalytic converters have many problems to solve air pollution, but it has given rise to other issues such as those raised by the EPA (Environmental Protecion Agency). According to the EPA, although the catalytic converter has been successfully convert nitrogen oxides to nitrogen and oxygen, but sometimes can form nitrous oxide compounds, N_2O. It is a factor that can cause global warming, 300 times higher than carbon dioxide (Wald 1998).

Concentrations of platinum group elements in the environment depends on several factors. Among the factors that affect the concentration of this element in the environment is the age of a catalytic converter, the catalyst over the age of 10 years have a higher propensity to free catalyst (Lesniewska et al., 2004), vehicle speed and traffic density also affects the concentration of this element in the environment (Ely et al., 2001).

Platinum emitted by vehicle exhausts not only in the form of metal, but also in the form of oxides, chlorides and bound in hydrocarbons. Rhodium is also released in the form of oxides (Moldovan et al., 2002).

Platinum group elements released from vehicle exhaust will spread to the surface of the road and may be combined with the corresponding road dust. Then the metal is likely to be attached on the surface of leaves and plants that are around the road. Metal will be taken by environmental agents such as water, then into the drainage system, settle in sediments and may be absorbed by the soil in the area. If the metal is easily soluble in water, it means that this metal may be absorbed by plants when the plants absorb water containing the dissolved metals. When the platinum metal content is too high it can cause a contamination of the plant. It is also dangerous if people are directly exposed to dust containing these metals, platinum inclusion in the food chain and the inclusion of platinum through respiration (Hidayah 2004).

Review of Related Theories

Due to the amount of use catalytic converters in various countries today, it has been many studies conducted on catalytic converters, platinum group element concentrations in the environment and the effects caused by these metals to the environment. The study involved about appropriate and effective way to investigate the presence of platinum group elements in the various samples, such as samples of road dust, water, sediment, plants and metal content is absorbed by aquatic animals.

Have been numerous studies done to determine the content of platinum group elements where the research using a variety of techniques, but the most widely used technique is the technique of mass spectrometry-induced coupling plasma (ICP-MS). This is because ICP-MS has kesensitivitian high level so as to achieve the reading to ppb (parts per billion). But there are also many techniques practiced in determining the content of platinum group elements, such as using neutron activation analysis (NAA) and atomic absorption spectrometry (AAS) (Barefoot, 1999).

The objective of the study of catalytic converters dilakukannnya generally is to examine the effect of a platinum group metal dust released by the catalytic converter on human health and other organisms. It also aimed to determine the effective rate of catalyst, the catalyst is to reduce pollution to improve the catalytic converter industry (Palacios et al., 2000).

The study was done in Munich reported that they found the concentration of platinum group elements in the sample, which means that there are plants in the vicinity of a busy road. Other studies also reported that Pt and Pd concentrations of elements that have been found to be high in many environmental samples, are not limited to elements that are exposed on the road only (Heinan 1999).

In one study, we found 5 µg platinum group elements are released for each kg that was used in the catalytic converter. There is also a cubic meter of exhaust at 100 km per hour, can contain up to 15 ng / kg of platinum group elements (Heinan 1999). Studies have also been done on the road in the land of Hong Kong who found that concentrations of the elements Pt, Pd and Rh of 160 ng / g, 107 ng / g and 34.5 ng / g for each (Pan et al., 2009).

From the results obtained from the studies that have been done show that there is an increased concentration of platinum group elements into the environment. A study shows that an increased concentration of platinum metals in soil samples tested within 8 years. Where ever the metal concentrations as high as 70 times higher than background levels, "background level". Samples of grass were planted at various sampling sites, in a certain range and have different traffic densities. Results from this study showed, in the range of 0.8 to 2.9 µg / kg / dm from the road, the concentration of platinum group metals are taken by grass grown is the highest, with

high traffic density. Whereas in grass samples grown on low traffic density locations, platinum metal content of grass is taken by the highest in the range of 0.2 to 0.5 µg / kg / dm from the road (Barefoot, 1999).

The study of platinum group elements found in street dust in the tunnel have been carried out in Malaysia. Nik (2006) have successfully detected the presence of Pt and Rh metal in the tunnel but did not find the presence of Pd element. It also compares the readings found in the tunnel that is not in the tunnel and it was found that the Pt content in the tunnel is higher than that is not in the tunnel.

From the results of the study that was done it was found that most of the platinum group elements in the environment is derived from the diguanakan catalytic converters in vehicles. Studies have also shown that the transfer of platinum group elements are inert, not easy to move and just move on water and wind assistance. However, there is still a platinum group elements in plants. It proves that the platinum group elements are absorbed into the plant even in small quantities.

However, until now there has not been any impact on the people associated with platinum group elements. This is because the concentration of platinum group elements are still very low so it is not a significant impact on humans. However, people should still be careful because it is currently more popular catalytic converters used on vehicles, allowing the platinum group elements will be present with more on the environment and can be harmful to humans.

Research Methodology

This study was conducted at 4 stations UKM Engineering Lake where 4 stations 1 station each taken two samples of soil and grass. UKM engineering lake close to the road to allow the contents of platinum group elements. Here is the location and sampling stations were chosen:

Fig. 1. UKM Engineering Lake *(Source: Google Map)*

1) Station A (02˚55.504'U; 101˚46.346'T)
• A.1: Grass
• A.2: Soil
2) Station B (02˚55.446'U; 101˚46.326'T)
• B.1: Grass
• B.2: Soil
3) Station C (02˚55.396'U; 101˚46.370'T)
• C.1: Grass
• C.2: Soil
4) Station D (02˚55.466'U; 101˚46.371'T)
• D.1: Grass
• D.2: Soil

Grass Samples

Plant samples taken soaked and then washed using distilled water to ensure the leaves and shoots of grass free from dust, dirt, dust or other foreign material stuck in the grass.

After sample clean from dirt, it is dried in an oven at a temperature of 80C until completely dry, at least for 2 days for each sample. Dry samples were ground using a mill until the grass completely destroyed. Grass samples were then crushed in a sieve using a laboratory sieve size of 500 m.

Samples of grass and then digested using aqua regia solution, whereby each 0.1 gram sample of grass weighed and put into a special container, then mixed with aqua regia solution (4 mL HNO3: 6 mL HCl) fumes in the chamber and then inserted into the Microwave Digestion System Start D for approximately 1 hour. After approximately 1 hour the sample was removed, filtered and add distilled water up to 100 mL. Filtrate stored in sample bottles for analysis.

Soil Samples

The soil samples were taken and dried in an oven at a temperature of 80C for 2 days, after dry land then pounded and sifted using a sieve size of 500 m laboratory. After getting a soil sample size of 500 m and then weighing the sample of 0.1 grams park in special containers and digested using aqua regia solution (4 mL HNO3: 6 mL HCl) fumes in the chamber and then inserted into the Microwave Digestion System Start D for about 1 hour . After approximately 1 hour the sample was removed, filtered and add distilled water up to 100 mL. Filtrate stored in sample bottles for analysis.

Standard Solusion

Standard solution used in this experiment is Multi-element ICP-MS Std 3 experiments conducted to detect the elements present in the soil and grass samples using ICP-MS is a form of analysis of the total quantity (Total Quant Analysis).

Research Findings

Analysis of all samples is done using ICP-MS, ELAN 9000 model method used in this analysis is the method of "total quantity" which is a rough analysis of metal that can analyze 83 elements in a sample at a time.

Grass Samples

From the results obtained, it was found that only the rhodium metal that can only be detected, albeit only at 2 stations in the UKM Engineering Lake. While reading for platinum and palladium metals were not detected at any station. This occurs because the concentration of platinum and palladium metals are below the detection limit.

The metal content in the grass Rh overall highest found at station A (02˚55.504'U; 101˚46.346'T) UKM Engineering Lake closer to the road than the other stations, with a concentration of 15 225 µg / g ., while at station B UKM Engineering Lake is 1770 µg / g. At the other stations did not show the presence of rhodium reading, because reading this rhodium at other stations were below the detection limit.

Studies done on the highways of Australia, including minor roads by Ely et al. (2001), showed that the rhodium content in grass samples (washed permukaannnya), which is 0 meters away from the road of 0.0001 µg / g. This indicates that the rhodium content found in samples of grass in Australia a little more than that found in UKM Engineering Lake.

The presence of Rh metal is supported by studies Hidayah (2004), in which only metal Pt and Rh only detectable, due to the ratio of Pd metal used in catalytic converters fewer than metals Pt and Rh. In addition, also due to the absence of metallic Pt and Pd, Rh metal is lighter than metal Pt (Jarvis et al., 2001).

Soil Samples

From the results obtained, it was found that only the rhodium metal that can only be detected, at 3 stations in the UKM Engineering Lake, while reading for platinum and palladium metals were not detected at any station. This is due to the concentration of platinum and palladium metals are below the detection limit.

Rh metal content in the soil at the height of the station C (02˚55.396'U; 101˚46.370'T) Lake Engineering UKM little far with the road compared to other stations but the proximity to the construction site of the new building of the concentration of 9.579 µg / g, while at station A UKM Engineering Lake of 8.421 µg / g and station B Lake Engineering UKM is 2.347 µg / g.

Studies have also been done on the road in the land of Hong Kong which found that rhodiumnya content lower than that found in UKM Engineering Lake of 0.0345 µg / g (Pan et al., 2009).

Others Metal

Apart from analyzing the platinum group metals, the analysis of other metals were also carried out. A total of 80 other elements can be detected in all samples of H, He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Ru, Ag, Cd, in, Sn, Sb, Te, I, Xe, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Au, Hg, Tl, Pb, Bi, Th and U. But only a few heavy metals associated with vehicle activity only taken note, the elements Cu, Zn, Ni and Pb.

Conclusion

Based on the results of the research that has been done, it was found that rhodium can be detected from samples of soil and grass. In this study could not detect the presence of platinum and palladium metals, is because the concentration of platinum and palladium metals are below the detection limit. This may be caused by the distance between sampling locations with long road to platinum metal has not reached the sampling location and also because the road cleaning up metal platinum can go to other places and also Rh metal is lighter than metal Platinum.

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