ENHANCED CHEMILUMINESCENT TECHNIQUE AS A SCREENING TOOL FOR AIRBORNE HEAVY METALS

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ABSTRACT. *The chemiluminescent technique advocated in this paper a free radical reaction based upon oxidation of luminol in the presence of the enzyme horseradish peroxidase and an enhancer such as p-iodophenol. This analysis has shown that, the technique is less sensitive to detect the presence of* Mn^{2+} *and* Cu^{2+} *in the dew and rain samples (correlation coefficient=0.0065) for both detectors. However low intensity of light emission and recovery curves was obtained from dew and rain samples from the polluted compare to the non – polluted area.*

INTRODUCTION

Preliminary studies in monitoring sewage effluent using chemiluminescent technique, showed a good correlation with the existing monitoring techniques such as Biological Oxygen Demand and Chemical Oxygen Demand. The correlation coefficients were 0.91 and 0.96 respectively (Billings *et. al*, 1994 and Sawcer, 1999). These early works encouraged the potential use of chemiluminescent technique for monitoring effluent discharges and pollution tracing including the concentration of heavy metals in the environment.

Many studies have been carried out to investigate and determine the concentration of heavy metals in the environment because of their potential to become highly toxic compounds. These studies were conducted, using a complex procedure and very expensive instruments. A cost-effective, rapid, sensitive and a simple screening tool is needed to monitor the concentration of heavy metals and other pollutants in the environment. Therefore this studies is aiming to investigate the application of chemiluminescent technique as a screening tool for monitoring of manganese and copper in the dew and rain samples.

MATERIALS AND METHODS

The reaction is based upon the oxidation of luminol (chemiluminescence molecule) in the presecence of an enzyme (horseradish peroxidase) and an oxidant (sodium perborate). An enhancer (4-Iodophenol) was used to obtain a stable , high intensity and prolonged light emission for detection. The light emission is measured using inexpensive photodiode detectors or photomultiplier-based instruments for 4 minutes. The light emission from the environmental sample which have been treated with these reagents was compared with the a similar reaction using a deionised water control sample. The information about the nature and degree of contamination is based upon the proportion of light inhibition and the shape of recovery curve.

Sampling

Sampling was conducted in fall term with most of the days are cloudy with temperatures around 13^0C to 24^0C and raining on 9, 11, 31^{st} of July and 1^{st} of August. Rain was collected using a glass and a saucer. Whereas, the automatic machine dew collector and manual system were used to collect the dew samples. Winterbourne Garden (WG) is a rose garden and Wolfson Building (WB) with heavy traffic activities were the two places, which selected as the non-polluted and polluted area for this study.

Instrument

Two types of detectors were used in measuring the chemiluminescence light emission, Bio-Orbit 1250 Luminometer (BO) and Portable Silicon Photodiode Luminometer (PB). The BO was linked to a computer running Bio-Orbit software, which plotted the course of light emission and calculated the intergral of the curve for 4 minutes. The PB is a battery powered handheld luminometer and is used to measure the light produced by chemluminescence and bioluminescence within the range of 300 – 900nm.

Materials

All reagents including the horseradish peroxide buffer, assay buffer and signal solution were prepared as explained by Sawcer, 1999.

Copper and Manganese analysis

The concentration of Mn and Cu in the dew and rain samples was detected using AAS. The same concentration was prepared in deionised water and were analysed with the BO to determine the integral value and the recovery curve for both metals

RESULTS AND DISCUSSION

Rain samples

A similar intensity and shape curve, from the WG rain sample (Figure 1) with the reference have been recorded by the two luminometers. However, rain sample from the WB (Figure 2) gives an s-shape curve, which suggesting a different entity in both samples and it is more contaminated compare to the WG samples.

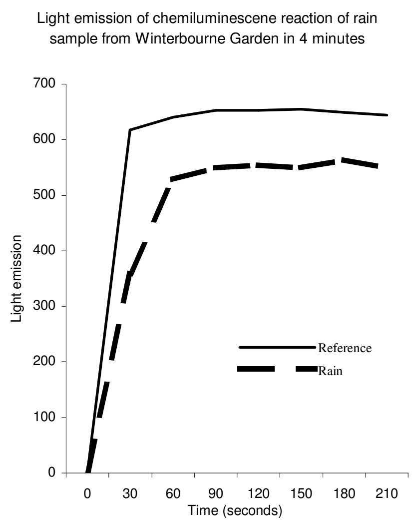

Figure 1: The recovery curve of chemiluminescence of rain sample from Winterbourne Garden (WG).

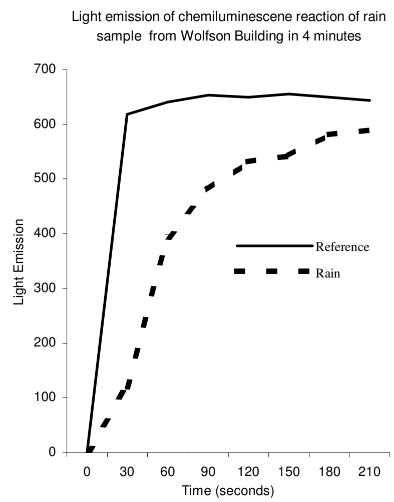

Figure 2 : The recovery curve of chemiluminescence of rain sample from Wolfson Building (WB).

Dew samples

The recovery curve of the dew samples, shows a typical pattern for both detectors (Figure 3 and Figure 4). The morning dew from the automatic machine dew collector (AMDC 1) has a lower curve compared to the afternoon dew (AMDC 2). A similar pattern has been obtained from the manual system dew collector (MSDC) either from the morning (MSDC 1) or the afternoon sample (MSDC 2). The dew recovery curves also show lower light emission than the rain sample.

Dew is formed in relatively small volumes, captures and concentrates the gaseous and/ or particulate pollutants of the local area more, compared to the rain (Kobayashi *et al.*, 2002). Major ions such as SO_4^{2-}, HCO_3^-, NH_4^+, Mg^{2+}, heavy metals (Mulawa, *et al.*, 1986) and highly soluble gaseous eg. HNO_3, HNO_2, HCOOH and CH_3COOH (Farmer and Dawson, 1982) in the dew, can inhibit the light emissions from the chemiluminescent reaction.

Moreover, the concentration of radical species such as OH*, are greater in dew and capable of forming hydrogen peroxide and organic peroxides (Arakaki, *et al*., 1998). These radical species cause low intensity of light emission by quenching the flux of enhancer radicals before they react with the luminol (Sawcer, 1999).

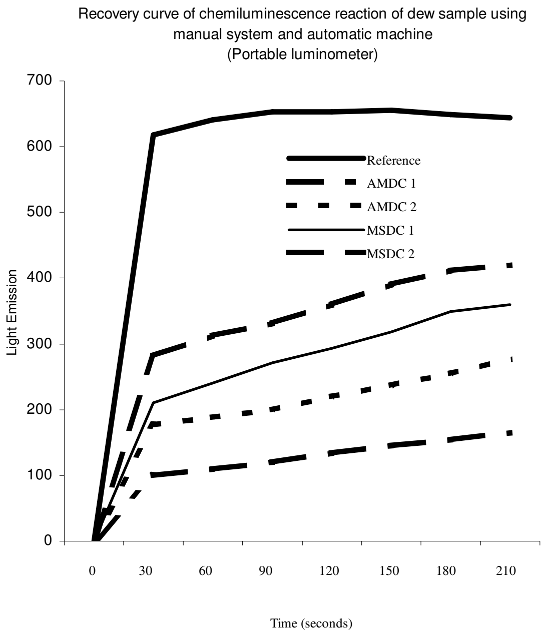

Figure 3: The recovery curve of chemiluminescence reaction of dew sample using the Portable luminometer (PB).

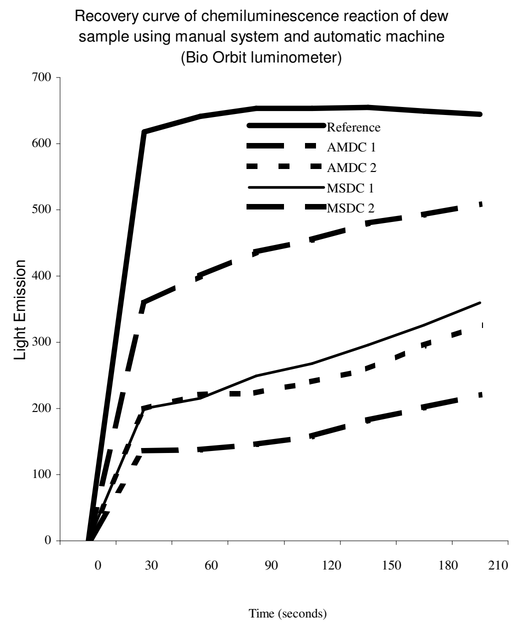

Figure 4: The recovery curve of chemiluminescence reaction of dew sample using Bio Orbit luminometer (BO).

Sensitivity of Both Detectors

There are many factors that influence the light emission and the recovery curves obtained from the samples. This can be minimised by using a volume of sample, which gives a percentage of inhibition between the range of 20 – 80 %. Although both of detectors have different sensitivity, still a good positive correlation are shown on the Eclox Unit from WG and WB between the two detectors (0.70 and 0.75). This shows that both detectors can be used as a screening tools for rain and dew quality with equal confidence. However, the PB has more advantage as it is portable, energy efficient, simple to operate and it gives rapid results. More over, it can be carried out for field analysis than the BO, but the curve analysis has to be plotted manually.

Manganese and Copper

The low concentration of copper (Cu) and manganese (Mn) in the dew (2 µg/l and 1.25 µg/l), gives a parallel curve shapes with the reference even when the analysis was run in higher concentration for extended times (Figure 5 and 6).

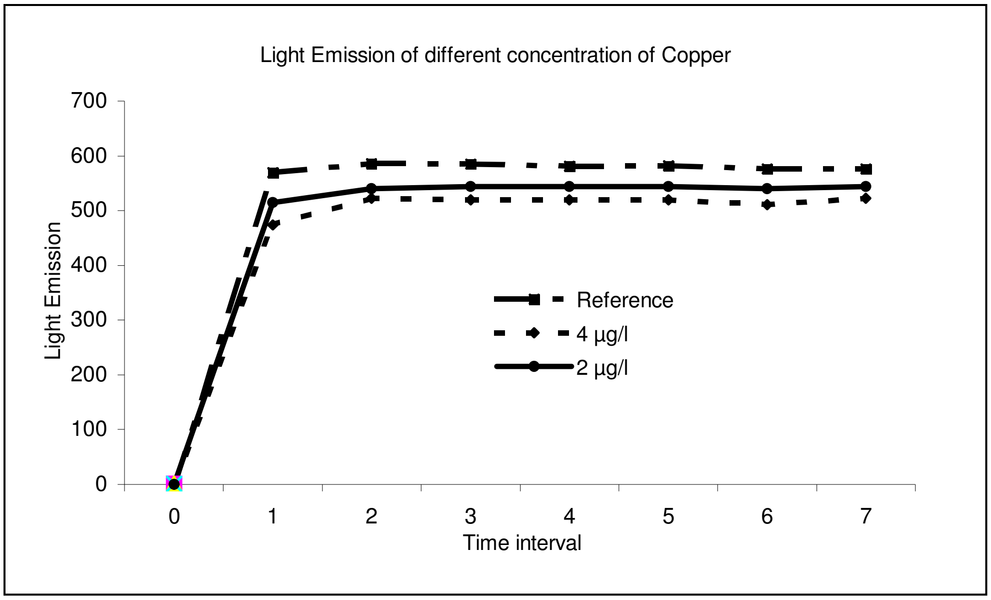

Figure 5: The recovery curve of chemiluminescence reaction of copper in dew with different concentration using the Portable luminometer (PB).

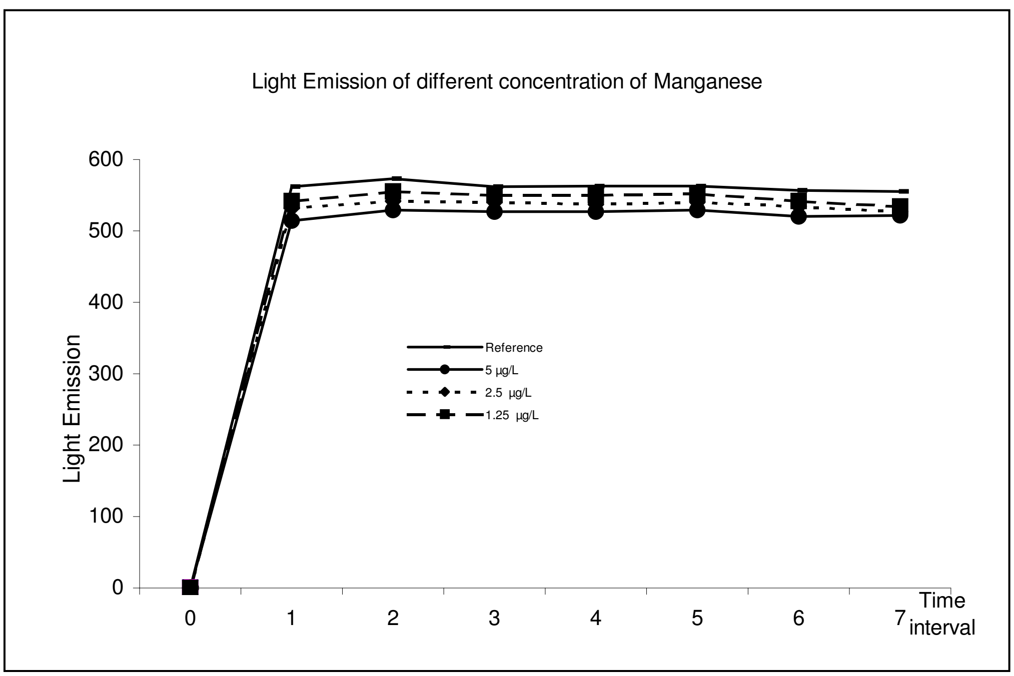

Figure 6: The recovery curve of chemiluminescence reaction of manganese in dew with different concentration using the Portable luminometer (PB).

These indicate that both metals are not the major inhibitors of the light emission.

CONCLUSION

Analysis of dew and rain with chemiluminescence provides a potential good screening method for monitoring air pollution locally. There are many entities in dew and rainwater that will influence the light emission from the chemiluminescence reaction. Therefore, further studies are needed to know exactly what are the specific causes of the differences, as the chemiluminescent is more a non-specific, screening tool.

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