

THE INDIRECT ANALYSIS OF MANGANESE FROM ENVIRONMENTAL SAMPLES OF MINES AND RIVERS

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(Key words : Manganese, Environmental samples, Mines, Sediment)

INTRODUCTION

Manganese is a relatively abundant element, naturally found in rocks, soil, water and food, and consisting approximately 0.1% of the earth's crust [1]. Owing to its numerous oxidation states (+2, +3, +4, +6 and +7), manganese forms various compounds with distinct colors, making it an interesting subject to study about. Moreover manganese and its compounds have extensive applications in science. Manganese is mainly used in alloy steels, while its compounds are used, among other things, as catalysts and powerful oxidizing agents.

This study reports on the indirect analysis of manganese in environmental samples collected from mines and rivers. A site in Kamiyama town, about 50 km West of Tokushima City, was chosen for this study. Samples were collected from a hill (mine slag) and its neighboring stream, the Hiroishidani river. Three sampling sites were identified, and given arbitrary names Fish site, Mine site and Blue concrete site. Figure 1, produced by Hahashi et.al [2], gives a sketch diagram of the area under study.

Most noticeably about the stream is that the Fish site is inhabited by fish species something not observed at the other two sites, hence the name Fish site. The Mine site, so named because of the mine slag, is characterized by blue and grey sediment, where the blue sediment is indicative of adsorbed Cu (II). Down stream, the presence of Cu (II) is even more clearer on a concrete wall (modified river bank) at the Blue concrete site. For comparison pur-

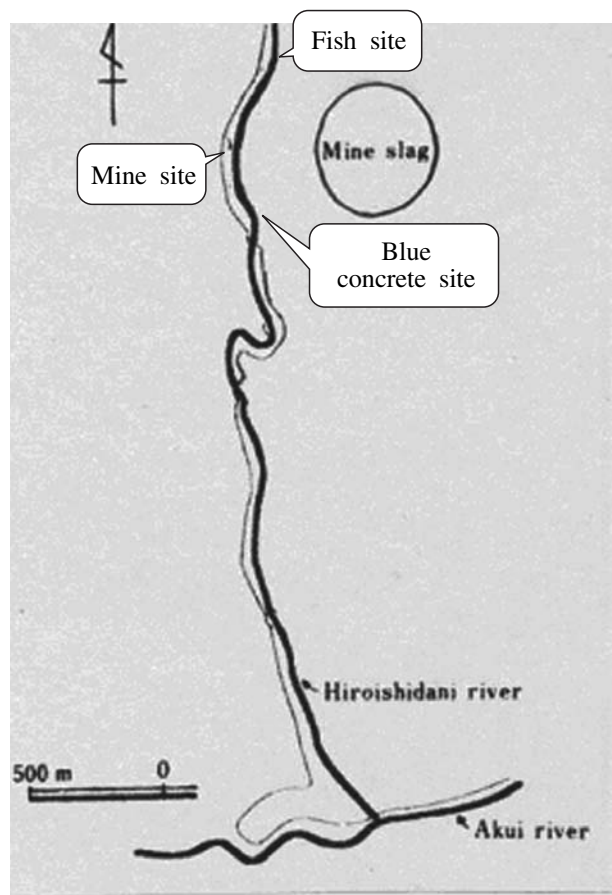


Figure 1: A sketch map of the sampling site (produced by Hayashi et.al [2])

poses, further sampling was done from the Yoshino river at the 10th Dam site.

Prior studies show that the river's surface water contains trace amounts of copper (less than 1 ppm) and that the copper is introduced in the river through the leaching of a colorless solution from the hill [2].

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EXPERIMENTAL

Scientists perform the direct analysis of manganese through atomic flame emission spectrometry. In this study, an indirect analysis of manganese was explored as shown by Figure 2. Here, manganese was first oxidized to permanganate complex, MnO_4^- . The equivalent amount of manganese was then calculated from measured concentration of the permanganate ion solution.

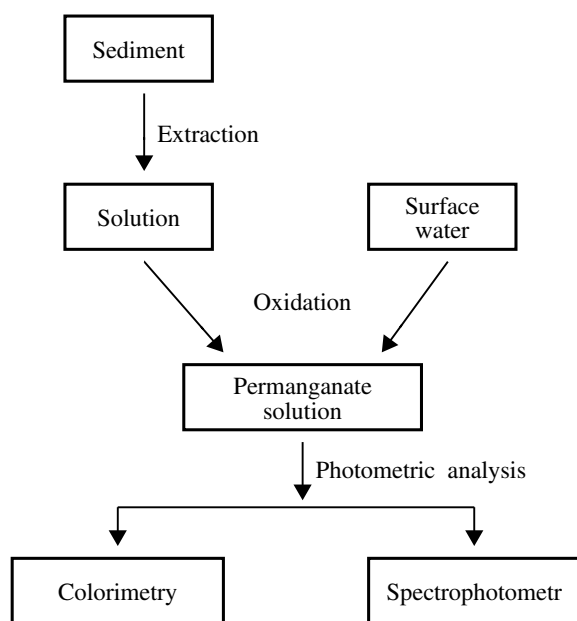


Figure 2: The analytical scheme of manganese.

In total, 16 samples were analyzed, 11 from the river, 2 from the hill, 2 from the 10th Dam and 1 from the colorless solution that is leaching from the hill into a clay reservoir at the edge of the river.

EXTRACTION

Procedures were simplified from those by sangyo tosho publishers [3]. To a measured quantity of sample (0.1~0.5g sediment) in a 200 ml beaker, 10 ml of concentrated nitric acid and 20 ml of concentrated hydrochloric acid were added. The beaker was covered with a watch glass and the mixture boiled until the brown fumes were expelled. A further 20 ml of concentrated nitric acid was added and the mixture was again boiled to expel the brown fumes. After cooling to room temperature, the inner surface of the beaker was washed with about 50 ml of distilled water and the mixture boiled for a minute. The warm solution was carefully filtered in a

clean 200 ml beaker and the sediment washed with about 2 ml aliquots of hydrochloric acid (1:10) for 2 to 3 times. With the beaker uncovered, the solution was boiled until about 2~3 ml remained. The inner surface of the beaker was again washed with 10 ml of hydrochloric acid (1:10), the solution warmed and about 50 ml of distilled water was added. Extraction was then followed by the oxidation procedure.

For the analysis of surface water, 100 ml sample was transferred to a 200 ml beaker. It was then boiled until about 2~3 ml remained. The inner surface of the beaker was washed with 10 ml hydrochloric acid (1:10), boiled for a minute and about 50 ml of distilled water was added. This was then followed by the oxidation procedure.

OXIDATION

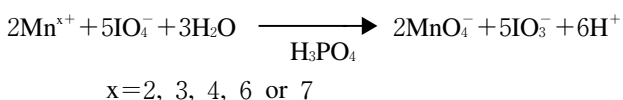
To a sample solution, 0.5 g of potassium periodate and 3 ml of 85% phosphoric acid were added. The beaker was covered with a watch glass, the solution boiled and kept at the boiling temperature for at least 3 minutes. After cooling to room temperature, the solution was transferred to a 100 ml volumetric flask and diluted with distilled water to the mark. After mixing, the color intensity was compared with that of potassium permanganate standard solutions and the absorbances measured using a Double-Beam spectrophotometer, at a wavelength of 525nm. These procedures were simplified from those of Kolthoff and Sandell [4].

PREPARATION OF STANDARD SOLUTIONS

Accurately weighed amounts of potassium permanganate standardized samples, were transferred in 200 ml beakers to prepare 0, 10, 20, 30, 40, 50 ppm of standard solutions. 75 ml sulphuric acid (1:4) was added in each beaker and the solids completely dissolved. In each beaker, a solution of chloride-free sodium sulphite (Na_2SO_3) was added, drop by drop, until the solution was decolorized. The solution was boiled to expel sulphur dioxide and this was then followed with the oxidation procedure. Permanganate solutions prepared this way (containing excess of periodate) are stable indefinitely.

RESULTS AND DISCUSSION

The equation below shows the balanced chemical equation for the oxidation reaction. It is based on the oxidation of manganese to the violet permanganate complex, using potassium periodate in a hot acid solution.



Phosphoric acid must be present in the solution to prevent the precipitation of ferric periodate and iodate, and to decolorize cations, like ferric and cupric ions, through complex formation.

A linear relationship was obtained when absorbances were plotted versus the concentrations of standard solutions. Beer's law, $\log I_0/I_t = + \epsilon c l$, was therefore obeyed.

From the slope of the plot, the molar extinction coefficient, ϵ , was found to be $2497 \text{ cm}^{-1}\text{M}^{-1}$, (M is molarity of the solution in $\text{mol}\cdot\text{dm}^{-3}$). Untreated potassium permanganate standard solutions (i.e. without treatment with a sulphite) gave a molar extinction coefficient value of $2449 \text{ cm}^{-1}\text{M}^{-1}$, a value comparable with the reported figure of $2455 \text{ cm}^{-1}\text{M}^{-1}$ [5]. Using the plot, the amount of manganese at various sampling sites was calculated.

SURFACE WATER

In general, the amount of dissolved manganese in surface water was very low, and thus could not be efficiently detected by the simple techniques studied in this research. Samples from the 10th Dam site and the Fish site showed no manganese content or very low concentrations that were below the detection limit of this simple analysis. In contrast, surface water from the Mine site indicated much higher concentrations of dissolved manganese, 0.13 ppm.

The colorless solution leaching from the hill, had the highest content of manganese, 6.41 ppm. Down stream at the Blue concrete site, the color of the permanganate ion solution was too dilute for accurate measurement.

The fact that manganese was not be detected or was very low upstream, high near the mine slag and

low downstream, suggests that manganese is introduced into the river by the mine slag. The old mine, therefore, pollutes the river through the leaching of minerals from it.

Clearly, the products of this hill might be the major contributors to the observed behavior of aquatic life in this stream. Fish is present upstream, but probably cannot survive from the Mine site downstream because of high concentrations of minerals (manganese, iron and most notably copper). However, the amount of manganese in surface water could differ for different sampling sites, depending on factors like the water's pH and turbidity of the river.

SEDIMENT

Figure 3 represents the highest amount of manganese detected at each sampling site. It shows that the sediment from the 10th Dam, the reference sample, contains 0.117% manganese.

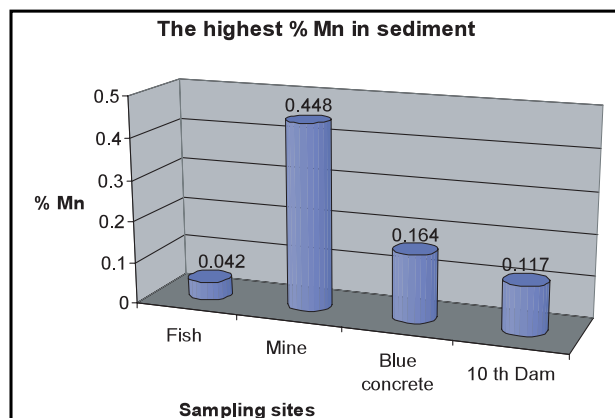


Figure 3: The highest amount of manganese at each site

It is interesting to note that sediment from the Fish site, upstream, contains the lowest amount of manganese (0.042%) of all sites studied. The amount of manganese in the sediment from the Mine site is the highest (0.448%), and it decreases to almost one-third at the Blue concrete site (0.164%). These results agree with those obtained in the case of surface water. In both cases, manganese content is zero or very low at the upstream, highest near the hill and low down stream

Figure 4 compares the concentration of manganese in sediment collected from the mine slag and

the river.

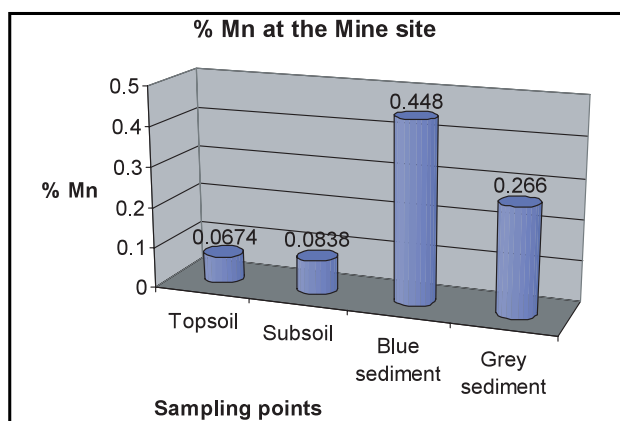


Figure 4: The amount of manganese from the mine slag and the Hiroishidani river

This figure shows that, apart from copper, the hill also has trace amounts of manganese, 0.0674% (topsoil) and 0.0838% (subsoil). The river's sediment contains about three times (0.266% from the Grey sediment) and 5 times (0.448% from the Blue sediment) more manganese than the mine itself.

Both Figures 3 and 4 suggest that high concentrations of manganese can be found in the vicinity of the site where it is produced, the Mine site in this case. Manganese is introduced in the river through the colorless solution. However, on entering the river's surface water, it is converted to a residue that settles out of the water. Possible explanations for this may include, among others, the adsorption of the dissolved manganese to sediment and the oxidation of this mineral by atmospheric oxygen to oxides like MnO , MnO_2 or Mn_2O_3 .

Within the same site, there is a vast variation in the concentration of manganese. At the Mine site, for example, the amount of manganese in the blue sediment (copper rich sediment) is 0.448% and that in the grey sediment (normal sediment) is 0.266%.

This implies that the rate, at which copper and manganese are either oxidized to insoluble residues or adsorbed to sediment, is the same. Further research is necessary for confirmation.

CONCLUSION

This research confirmed that in general, surface water contains only trace amounts of dissolved manganese. High concentrations could, therefore, be due to human activities such as industrial spillage and mine dumps, and improper waste management of technological products like dry cells and steel. The Fish site and the 10th Dam site are examples of environmentally healthy rivers. Conversely, the Mine site represents a river that has been polluted by human activities, mining in this case.

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ABSTRACT

This study reports on an indirect analysis of manganese from environmental samples of an old copper mine and its neighboring river. Sediment and surface water were analyzed for the presence of manganese. Manganese was extracted, in the case of sediment, using aqua regia, followed by oxidation to the violet permanganate complex (MnO_4^-) with potassium periodate, in a hot acid solution. Analysis of the permanganate complex, by colorimetric and spectrophotometric analytical methods, shows that the river contains a relatively high amount of manganese near the mine, and that the presence of chemical pollutants, directly or indirectly affect aquatic life.

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