原著論文

DEVELOPMENT OF TEACHING MATERIALS FROM ENVIRONMENTAL SAMPLE OF MINES AND RIVERS

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抄録：この研究は鉱山とその付近の川の試料を用いた教材の開発について報告したものです。これは堆積物や表面水中のマンガンを間接的に求める研究であり，教育実践に適するように実験操作は高校生用に簡易化した。ここではマンガンを堆積物から抽出し，紫色の過マンガン酸塩（MnO_4^-）に酸化し，標準濃度の溶液と比色することにより試料中のマンガンの濃度を求めた。堆積物中のマンガン量は，過マンガン酸塩の濃度を対比させることにより求めた。授業実践を想定した生徒の活動を計画し，これを地元の鳴門高校の２年生40名に対して試みた。

キーワード：マンガン，鉱山，過マンガン酸塩，授業活動，高校生

Abstract：This study reports on the development of teaching materials by using samples from mines and their neighboring rivers. The indirect analysis of manganese in sediment and surface water was studied, and the procedures were simplified for high school learners. Here, manganese was extracted from sediment, oxidized to the violet permanganate (MnO_4^-) complex and the concentration of the complex determined by color comparison with standard solutions. The concentration of the permanganate complex was used as the relative measure of the amount of manganese in the sediment. The lesson activities developed and were tried to forty (40) grade 11 learners at Naruto high school, Japan.

Keywords：Manganese, Mine, Permanganate, Lesson Activities, High school learners

INTRODUCTION

Manganese compounds have extensive applications in science teaching. Compounds like, MnO_2 and $KMnO_4$, are widely shown in secondary school textbooks as being used as oxidizing agents, catalysts and in dry cells (Horn,1987,1988). Owing to its numerous oxidation states (+2, +3, +4, +6 and +7), manganese forms various compounds with distinct colors, making it an interesting subject for learners to study about. More over, manganese is a relatively abundant element, naturally found in rocks, soil, water and food, and consisting approximately 0.1% of the earth's crust (WebElements Periodic) (Bruce,J.,2002).

Scientists perform the direct analysis of manganese through atomic flame emission spectrometry, a technique that is too advanced for most amateur chemists. In this study, an indirect analysis of manganese was explored. Here, manganese was first extracted from sediment and then oxidized to the permanganate complex according to the following equation:

General knowledge

1. An oxidation reaction is: ① gain of electrons ② loss of electrons
2. A reduction reaction is: ① gain of electrons ② loss of electrons
3. Which has a bigger oxidation number between neutral Cu and Cu in CuO?
   ① Cu ② CuO

Properties of manganese

4. Name: Manganese:…………….(Name in Japanese)
5. Symbol:………….
6. Physical state: ① Solid ② Liquid ③ Gas
7. Color:…………………….
8. Classification: ① Metallic ② Non metallic
9. Give any compound(s) of manganese that you know: ………………………………
10. Give any use(s) of manganese or manganese compounds that you know:…………….

Table 1: Pre/Post activity questions

$$2Mn^{x+} + 5IO_4^- + 3H_2O \xrightarrow[H_3PO_4]{} 2MnO_4^- + 5IO_3^- + 6H^+ \quad (i)$$

x = 2, 3, 4 ,6 or 7

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.

METHODOLOGY

An old copper mine and its neighboring river, Hiroishidani river, in Kamiyama town, Japan, were chosen for this study. Samples were collected along the river from the Fish site (up-stream), the Mine site (adjacent to the mine slag), the Blue concrete site (further down stream) and the Hill site (mine slag). Most noticeable about the river is that the Fish site is inhabited by fish species, something not observed in the other two sites.

The lesson was composed of a number of teaching strategies like brain-storming, open discussions and hands-activities. A questionnaire was distributed at the beginning and at the end of the lesson. Table 1 shows a sample of the questions. The questionnaire's main purpose was to assess learners' prior knowledge on the properties of manganese and to verify if learning has taken place.

Since the extraction requires more time, it was done by the facilitator prior to the lesson. Learners had to proceed with oxidation and analysis.

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. The procedures were simplified from those of Kolthoff and Sandell (Kolthoff,I.M.,Sandell,E.B.,1952).

CHEMICAL FORMULA (化学式)	CHEMICAL NAME (化合物名)	OXIDATION NUMBER OF MANGANESE ATOM (マンガンの酸化数)	COLOR (色)
K_2MnO_4 (aq)	Potassium manganate solution (マンガン酸カリウム水溶液)	(a) MnO_4^{2-} $x+4\cdot(-2)=-2$ $x-8=-2$ $x=6$ Mn: +6	(b) green 緑
(c) $KMnO_4$ (aq)	Potassium permanganate solution (過マンガン酸カリウム水溶液)	(d) MnO_4^- $x+4(-2)=-1$ $x-8=-1$ $x=+7$ Mn: +7.	(e) perpol 紫

Figure 1: An extract from a student's worksheet

Standard solutions were prepared by the facilitator prior to the lesson. For simplicity, learners used the concentration of the permanganate ion as a quantitative measure of manganese content.

RESULTS AND DISCUSSION

1. ACTIVITY 1: POTASSIUM MANGANATE VS POTASSIUM PERMANGANATE

After brain-storming and discussion on the properties of manganese and its compounds, had to prepare dilute solutions of potassium manganate and potassium permanganate in test tubes, record the color of each solution and then calculate the oxidation number of the manganese ion in each compound. The outcomes of this activity were, mainly, to demonstrate the various oxidation states of manganese and the different colors of manganese containing compounds.

Figure 1 is an extract from a learner's worksheet. It was encouraging to note that some learners attempted to write their answers in both Japanese and English.

Also encouraging is that some learners showed how they calculated the oxidation number of the manganese ion.

2. ACTIVITY 2: INDIRECT ANALYSIS OF MANGANESE FROM ENVIRONMENTAL SAMPLES OF MINES AND RIVERS.

RESULTS (結果)

Sampling Site 採取場所	Group 班	Amount of Permanganate 過マンガン酸イオンの濃度(mg/l)(PPm)
Fish A site 魚の住む場所	12	
	2	5
	3	5
Blue C Concrete Site 青いコンクリート場所	4	5
	5	10
	6	10
Hiroishi D mountain 広石山	7	不明
	8	15
	9	15
	10	15

Figure 2: Learners' results

The focus of the activity was to demonstrate the relationship between aquatic life, fish in this case, and chemical pollution by using manganese as an example. Since the amount of manganese in the river' s surface water is very low, the highest being 0.13 ppm at the Mine site, this study alone cannot, therefore, conclude on the effect of manganese to aquatic life.

The biggest challenge encountered was that learners did not understand that the amount of manganese determined was from sediment, not from surface water. This could be due to the fact that learners did not perform the extraction themselves.

Figure 2 shows results that were obtained by learners, 9 groups are shown. Due to insufficient samples, the concentration of the permanganate ion from the Mine site was provided as 30 ppm. The result for group 11 was unfortunately not recorded on the sheet. Nevertheless, both groups 2 and 3 obtained the same permanganate ion concentration of 5 ppm in sediment from the Fish site. Groups 5 and 6 agreed that the concentration of permanganate ion in samples from the Blue concrete site was 10 ppm, group 4 recorded it as 5 ppm. For the Hill site all groups, except Group 7, recorded 15 ppm as their results. Group 7 was not successful in obtaining positive results, because of the precipitation of ferric periodate and iodate.

Although some learners' results were different from those expected, the activity was successful in achieving certain outcomes. Learners were able to execute the oxidation process and estimate the amount of permanganate ion in the samples. Further more, the origin of manganese and the environmental impact of the old mine was, to some extent, realized.

In future, there should be more explanation on how to estimate the concentration from standard solutions. Most importantly, care should be taken that enough phosphoric acid is added to prevent the problem of precipitation as experienced by Group 7. None the less, learners seemed to have enjoyed the lesson as revealed by the following comments:

I found that Mn has several oxidation numbers. Your lesson was very much exciting. It was my first time to see Mn. When I answered about the color of Mn, you said "may be grey", I was impressed. I want you to come and present another lesson again!

I think it (fish) can be used as an indicator (of chemical pollution) because fishes do not live in the place where the concentration of MnO_4^- is high. (The learner probably

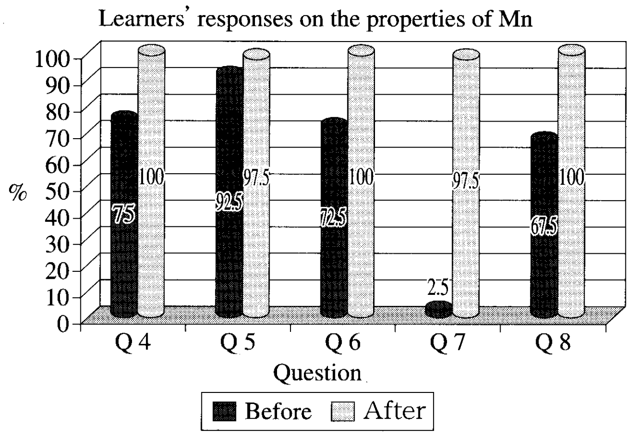

Figure 1: Learners' responses on the properties of manganese

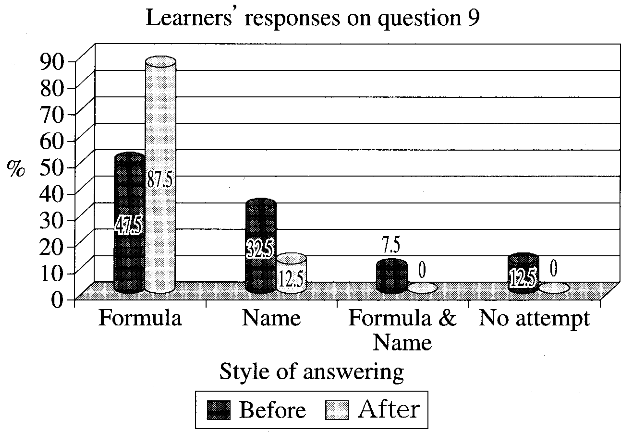

Figure 2: Learners' responses on manganese compounds

thought that Mn is present in sediment or service water in the form of the permanganate complex)

3. THE ANALYSIS OF THE QUESTIONNAIRE

3.1 REDUCTION AND OXIDATION PROCESSES (QUESTIONS 1, 2 AND 3)

Results show that in general, learners had a good understanding of the concept of oxidation and reduction processes.

3.2 PROPERTIES OF MANGANESE (QUESTIONS 4, 5, 6, 7, AND 8)

Figure 1 shows that, out of the 40 learners, 92.5% (37 learners) knew the symbol of manganese as Mn (Q5), but only 75% (30 learners) could write the name 'manganese' in Japanese (Q4). Results improved to 100% for the later and 97.5% for the former. As for questions 6 and 8, respectively, learners correctly classified manganese as solid, 72.5% (29 learners), and as metallic, 67.5% (27 learners). In both questions 6 and 8 the results improved to 100%.

Question 7, the colour of metallic manganese, was the most challenging question for learners. For this question, only 1 learner (2.5%), wrote the answer as grey. This suggests that, although learners knew about manganese, they never had the opportunity to see the real substance. Never the less, it is interesting to see the results improving to 97.5% (39 learners).

3.3 MANGANESE COMPOUNDS (QUESTION 9)

85%, 34 learners, knew certain examples of manganese compounds, with MnO_2 and $KMnO_4$ dominating the responses. The results improved to 100% after the lesson. Figure 2 shows that initially 47.5% (19 learners) gave the answer in a form of a formula and later the figure increased to 87.5% (35 learners).

Initially, 32.5% (13 learners) gave the answer in a form of a chemical name but after the lesson the percentage dropped to 12.5% (5 learners), 7.5% (3 learners) wrote both chemical formula and name, and 12.5% (5 learners) never attempted the question.

Apart from the improvement in results, it is also interesting to note that learners became more decisive. They all attempted the question and gave their responses either in a form of a formula or name. Arguably, this could be regarded as a positive sign that learners were active participants in the learning process. The increase in the use of chemical formulae at the expense of chemical name could be explained by the fact that the activity itself was dominated by formulae.

3.4 USES OF MANGANESE AND MANGANESE COMPOUNDS (QUESTION 10)

Although many learners had an idea about manganese compounds, fewer knew their uses. 57.5% (23 learners) gave dry cell and production of oxygen as answers and 35% (14 learners) never attempted the question. After the lesson, 38 learners (95%) gave correct responses. Of the 38 correct responses, 32 learners (84.2%) gave dry cell as an answer and 6 learners (15.8%) wrote both chlorine and dry cell as an answer. Not even a single learner mentioned the preparation of oxygen. This is probably due to the fact that the facilitator gave only the two written cases as examples.

CONCLUSION

While these activities shall improve learners' knowledge, values and skills in chemistry; they shall also sensitize learners, as members of various communities, on the importance of sustaining a healthy environment, with emphasis on water pollution. This will offer an opportunity to implement the UN's Education for Sustainable Development (Zakri,2004).

If properly planned, these activities would help to link the science theory with daily life experience. Research has shown that laboratory activities, does not necessarily enhance learners' understanding on how chemical principles affect their universe, the earth, its ecosystem, and the mechanisms of life (Hawkes,2004). These activities could therefore link the laboratory experiment with the environment and could help to create ideal conditions to introduce science knowledge in a 'natural'.

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