

Recoil Effects of Neutron-Irradiated Metal Permanganates

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중성자조사 금속 과망간산염의 반조효과

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Abstract

The chemical effects resulting from the capture of the thermal neutron by manganese in various crystalline permanganates, that is, potassium permanganate, ammonium permanganate and barium permanganate, have been investigated. The effect of pH of solvent on the distribution of radioactive manganese chemical species, that is, cationic ^{56}Mn , $^{56}\text{MnO}_2$ and $^{56}\text{MnO}_4^-$ produced in the permanganates by $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ reaction was studied by using various adsorbents and ion-exchanger, that is, zeolite A-3, kaolinite, alumina, manganese dioxide and Dowex-50.

The distribution of radioactive MnO_4^- in kaolinite and alumina has higher than that in other adsorbents and ion-exchanger at a representative pH value of 4, 7 and 9, respectively. The yield of radioactive MnO_4^- is higher at pH 4 and pH 9 than at pH 7.

The thermal annealing behavior of recoil manganese atoms produced in the permanganates by $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ reaction was also studied.

The retention of MnO_4^- in the thermal annealing is increased as annealing temperature increases when it was treated at 100°C and 130°C.

The recoil effect of permanganates was explained by the hot zone model.

요 약

과망간산염들, 즉 과망간산 칼륨, 과망간산 암모늄, 과망간산 바륨에서 망간의 중성자 포획으로 야기되는 화학적 효과를 고찰하였다.

$^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ 반응에서 생성된 방사성 망간 화학종, 즉 양이온 ^{56}Mn , $^{56}\text{MnO}_2$ 그리고 $^{56}\text{MnO}_4^-$ 의 분포에 미치는 용제의 pH효과를 여러가지 흡착제들과 이온교환체, 즉 제올라이트 A-3, 카올리나이트, 알루미나, 이산화망간 그리고 도엑스-50을 이용하여 고찰하였다.

카올리나이트와 알루미나에서 방사성 MnO_4^- 의 분포가 대표적인 pH값인 4, 7 그리고 9 각각에서 다른 흡착제와 이온교환체보다 높게 나타나며 동일한 흡착제일 경우에는 pH 4 및 pH 9에서가 pH 7에서보다 높게 나타난다.

$^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ 반응에 의하여 과망간산염에서 생성된 반조망간원자들의 열-어니어링 거

동 또한 고찰하였다.

열-에너지에서 $^{56}\text{MnO}_4^-$ 의 잔류율은 100°C 및 130°C 처리에서 온도가 높아질수록 증가함을 보였다.

망간염의 반조효과는 hot zone model로 설명하였다.

Introduction

Since the chemical effect of a nuclear transformation was observed by Szilard and Chalmers in 1934,¹⁾ numerous studies have been carried out in connection with the induced nuclear transformations in solid state.

In typical inorganic solids a 300 eV recoil event transfers energy to a region of 1000 atoms equivalent to a temperature of 1000°K for about 10^{-11} sec and in this region chemical reactions are possible between the recoil atom and the parent species, such as ligand bond breaking, ligand exchange, displacement, redox and bond reformation. These reactions do not have sufficient time to go to completion but are quenched by the cooling of the hot zone.²⁾

The retention, R , is the fraction of the total activity measured after the irradiation in the same chemical form as the target substance, and that can be considered to arise from four combination.

The first R_1 arises from nuclear events that fail to rupture the parent molecule; the second R_2 from events in which dissociation of the molecule is followed very quickly by reformation from largely the same constituent atoms; the third R_3 from reformation reactions involving hot product atoms; and the last R_4 from reformation processes involving thermalized product species. Thus the retention is following.

$$R = R_1 + R_2 + R_3 + R_4$$

The theoretical aspects of thermal annealing of radiation damage in solids were considered as annihilation through recombination of vacancies and interstitials following diffusive movement of

the species.³⁻⁵⁾

The analytic expression⁶⁾ for the mechanism shows that thermal annealing is a function of

$$t[D^0 \exp(-E/K_B \cdot T)] = t/\tau = D \cdot t$$

where t : heating time

D_0 : constant frequency term

E : energy of activation

K_B : Boltzmann constant

T : Kelvin temperature of heating

τ : Diffusive jump time in lattice equal to $D_0^{-1} \exp(E/K_B \cdot T)$

Adsorption phenomenon plays a significant role in the radiochemical analysis of recoil fragments. It is influenced mainly by the chemical properties of recoil species, their state in solution, the type of adsorbent and the nature of its surface.

The pH dependence of retention in permanganates has been studied by several authors to the variation of the adsorption of manganous on solid surface.⁷⁻⁹⁾

In this study the chemical effect resulting from the thermal neutron capture by manganese in different permanganates was investigated. The distribution of radioactive manganese produced was determined by using various adsorbents and ion-exchanger.

The effect of pH of solvent on the distribution of radioactive manganese produced in the permanganates was studied and the thermal annealing behavior of radioactive manganese was also studied.

Experimental

1. Materials

Potassium permanganate and barium perman-

ganate were of G.R. grade. Ammonium permanganate was prepared by the addition of ammonium chloride to a hot solution of potassium permanganate. The solution was filtered hot through a sintered glass funnel to remove manganese dioxide, and cooled immediately in ice. The crystal was twice recrystallized from doubly distilled water.

Manganese dioxide used as adsorbent was of C.P. grade. Alumina (E. Merck, Aluminium oxide 90, 70-230 mesh), kaolinite (Ward's Natural Science Establishment, Inc., U.S.A., 100-200 mesh), zeolite A-3 (Wako Pure chemical Industries, Ltd., Japan, 100-200 mesh) and Dowex-50 (Dow Chemical Co., U.S.A., Hydrogen-form, 100-200 mesh) were of chromatographic grade. The solvents of pH 4.7 and 9 were prepared by 0.01N-HNO₃ mixed with 0.01N-KOH. All other reagents used in the chemical procedure were of A.R. quality.

2. Neutron-irradiation and thermal annealing

About 3 mg of each permanganate was irradiated for three minutes with thermal neutron (neutron flux: 5×10^{12} n/cm² · sec.) in the TRIGA-mark III nuclear reactor at the Korea Advanced Energy Research Institute. The thermal annealing of permanganates was carried out by using a high-temperature oven, its temperature can be controlled within $\pm 2^\circ\text{C}$.

3. Separation procedure

Separation procedure, based on the method of Apers and Harbottle⁹⁾, is shown in Fig. 1. The neutron-irradiated permanganates were dissolved in solvents of different pH at room temperature and removed the radioactive manganese dioxide from solution by three-piece filter funnel. The radioactive cationic manganous ion was separated from the filtrate by shaking with 100 mg of each adsorbent for 30 minutes, followed by filtration.

The adsorbents containing radioactive manganese dioxide unremoved from the first step and manganous ion were washed with a solvent of pH 4, 7 and 9 until the purple color of permanganate

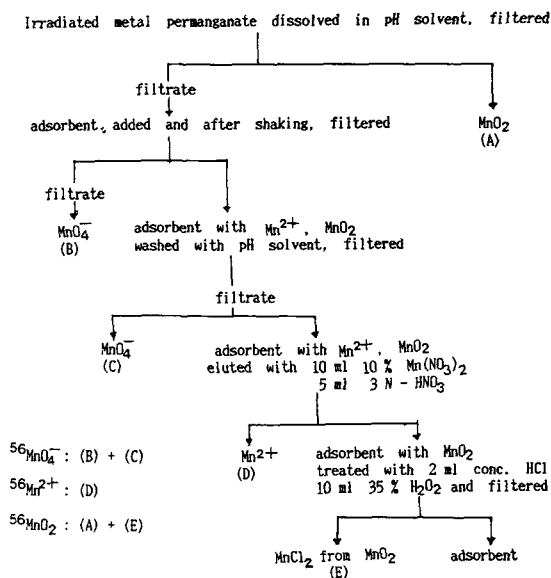


Fig. 1. Adsorption-Elution Procedure.

ion disappeared completely. The radioactive manganous ion adsorbed at the adsorbent was eluted with 10 ml of 10% manganous nitrate solution and then 5 ml of 3 N-nitric acid.

The fraction of adsorbent was reduced into a solution of manganous chloride by 2 ml of concentrated hydrochloric acid mixed with 10 ml of 35% hydrogen peroxide.

The thermal-annealed permanganates were dissolved in redistilled water and separated by using manganese dioxide, according to the separation procedure in Fig. 1.

4. Paper-electrophoresis

The separation of radioactive manganese was also carried out by paper-electrophoresis. The neutron-irradiated permanganates were dissolved in 0.5 N-nitric acid. The electrolyte was 0.1 N-nitric acid.

A strip of Whatman No. 1 filter paper, 40 cm long and 1.5 cm wide was wetted with the supporting electrolyte solution. The migration cell and the cover were cooled with ice-water by putting through a hole.

About 50 μl of neutron-irradiated permanganate solution was applied at the fiducial point of

Table 1. ^{56}Mn Activity Distribution(%) on Various Adsorbents in Neutron Irradiated KMnO_4 with pH of Solvent.

Yield pH Adsorbent	$^{56}\text{MnO}_4^-$ (%)			$^{56}\text{MnO}_2$ (%)			$^{56}\text{Mn}^{2+}$ (%)		
	4	7	9	4	7	9	4	7	9
Zeolite A-3	33.3±0.9	30.7±1.4	32.5±1.3	54.2±1.3	55.3±0.5	60.3±1.1	12.5±0.8	14.0±1.2	7.2±0.4
Kaolinite	45.6±1.3	40.7±1.2	44.2±0.9	51.5±1.0	49.5±1.4	51.0±1.2	2.9±0.3	9.8±0.2	4.8±0.2
Alumina	42.2±1.5	39.3±0.7	47.8±0.9	56.2±1.4	56.8±1.2	48.8±0.8	1.6±0.1	3.9±0.2	3.4±0.2
MnO_2	31.6±0.7	27.7±0.5	39.0±0.4	57.3±0.8	59.9±0.9	54.5±1.2	11.1±0.9	12.4±0.7	6.5±0.2
Dowex-50	19.7±0.2	17.2±0.3	19.0±0.8	47.0±0.7	52.6±0.4	52.9±0.6	33.3±1.0	30.2±1.2	28.1±1.4

Table 2. ^{56}Mn Activity Distribution (%) on Various Adsorbents in Neutron Irradiated KMnO_4 with pH of Solvent.

Yield pH Adsorbent	$^{56}\text{MnO}_4^-$ (%)			$^{56}\text{MnO}_2$ (%)			$^{56}\text{Mn}^{2+}$ (%)		
	4	7	9	4	7	9	4	7	9
Zeolite A-3	15.6±1.2	13.6±0.8	16.8±0.9	42.2±1.4	53.0±1.2	40.3±0.6	42.2±0.7	33.4±1.3	42.9±1.2
Kaolinite	61.3±2.0	58.9±1.9	62.5±1.4	30.4±1.3	38.2±1.6	29.4±1.5	8.3±0.8	2.9±0.1	8.1±0.3
Alumina	53.5±1.7	49.7±1.6	50.1±2.1	37.8±0.7	41.7±0.5	39.1±1.3	8.7±0.7	8.6±0.4	10.8±1.0
MnO_2	36.6±0.6	33.3±0.7	37.1±1.1	57.7±0.9	63.6±0.9	57.8±0.8	5.7±0.2	3.1±0.2	5.1±0.3
Dowex-50	14.3±0.1	12.5±0.2	13.5±1.0	34.8±0.9	34.7±0.6	31.8±1.3	50.9±1.8	52.8±1.7	54.7±1.4

Table 3. ^{56}Mn Activity Distribution (%) on Various Adsorbents in Neutron Irradiated $\text{Ba}(\text{MnO}_4)_2$ with pH of Solvent.

Yield pH Adsorbent	$^{56}\text{MnO}_4^-$ (%)			$^{56}\text{MnO}_2$ (%)			$^{56}\text{Mn}^{2+}$ (%)		
	4	7	9	4	7	9	4	7	9
Zeolite A-3	16.8±0.7	15.3±0.6	17.3±1.2	58.8±2.2	58.1±1.9	52.5±0.9	24.4±1.1	26.6±0.6	30.2±1.1
Kaolinite	36.1±0.6	31.9±0.9	36.0±1.3	39.4±0.9	48.1±1.5	46.2±0.8	24.4±0.7	20.0±1.4	17.8±0.7
Alumina	31.5±1.3	31.1±1.1	36.3±0.7	51.3±1.1	55.1±1.9	41.6±1.4	17.2±0.3	13.8±0.4	22.1±0.9
MnO_2	27.2±0.9	24.4±1.1	26.0±1.2	44.3±1.4	54.7±2.1	55.7±1.8	28.5±1.7	20.9±1.3	18.3±1.1
Dowex-50	24.7±0.7	14.6±1.1	29.5±1.3	52.7±2.3	54.5±1.6	42.6±0.9	22.6±1.3	30.9±1.4	27.9±1.3

the paper strip by using a lambda pipet.

The strip was covered with polyvinyl sheets. The electrodes were connected to the D.C. power supply, Toyo Model BA-8, Osaka, Japan, and a potential of 1000 volts was applied for 20 minutes.

After the electrophoresis run was over, the strip was removed from the migration apparatus, dried and cut into pieces of 1 cm length.

The radioactivity was measured by means of Polyspec Research spectrometer, single channel analyzer, connected with well type NaI (Tl) gam-

ma scintillation detector (1 × 3/4 in. × 2 in.), Baird model 810.

Results

The radioactive manganese activity distribution on various adsorbents in neutron-irradiated potassium permanganate, ammonium permanganate, and barium permanganate with pH value 4, 7 and 9 is shown in Table 1, 2 and 3.

The retention of the radioactive manganese as permanganates in potassium permanganate,

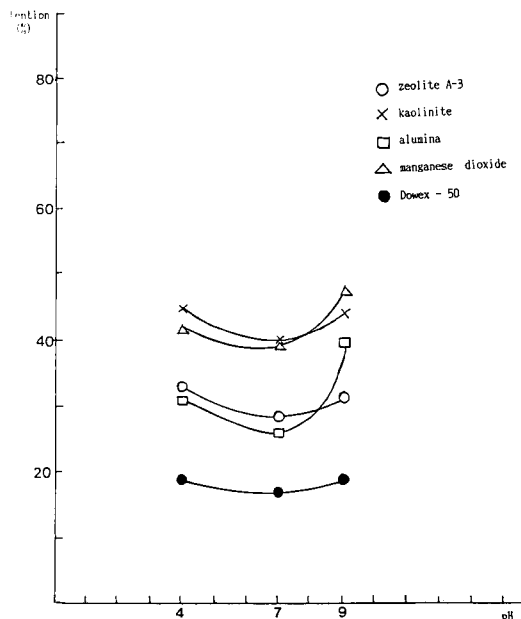


Fig. 2. Retention of $^{56}\text{MnO}_4^-$ on Various Adsorbents in Neutron Irradiated KMnO_4 as a Function of pH

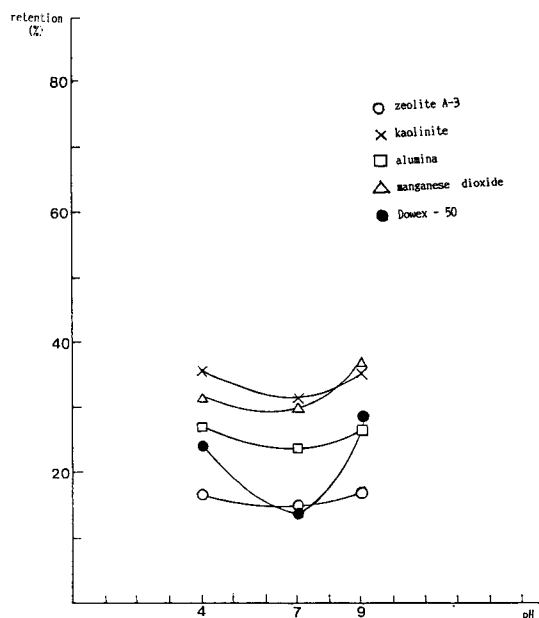


Fig. 4. Retention of $^{56}\text{MnO}_4^-$ on Various Adsorbents in Neutron Irradiated $\text{Ba}(\text{MnO}_4)_2$ as a Function of pH

ammonium permanganate and barium permanganate as a function of pH is shown in Fig. 2, 3 and 4. The yield of MnO_4^- increases at both low

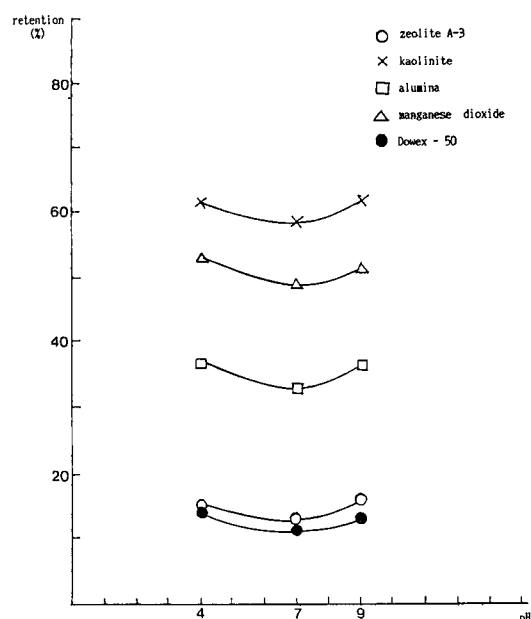


Fig. 3. Retention of $^{56}\text{MnO}_4^-$ on Various Adsorbents in Neutron Irradiated NH_4MnO_4 as a Function of pH

pH and high pH of solvent.

In kaolinite and alumina, retention is higher than in zeolite A-3, manganese dioxide and Dowex-50.

The chemical distribution of the radioactive manganese recoils in permanganates non-annealed and annealed at 100°C and 130°C for 60 minutes are shown in Table 4.

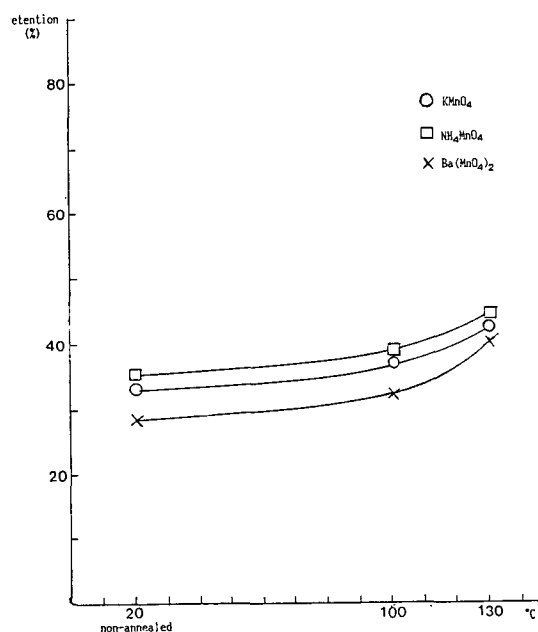
The annealing curves for the radioactive manganese recoils in neutron-irradiated potassium permanganate, ammonium permanganate and barium permanganate are shown in Fig. 5.

The retention increases when thermal annealed and also increases with annealing temperature increase.

The paper-electrophoresis histogram of neutron-irradiated ammonium permanganate is shown in Fig. 6. At the fiducial point, there is a large un-moving peak due to $^{56}\text{MnO}_2$ while the anionic $^{56}\text{MnO}_4^-$ peak and cationic $^{56}\text{Mn}^{2+}$ peak are appeared at the distance of 7 and 9 cm from fiducial point towards anode and cathode, respec-

Table 4. Chemical Distribution (%) of ^{55}Mn Recoils in Permanganates Non-Annealed and Annealed at Two Temperature for 60 min. (Adsorbent: Manganese Dioxide)

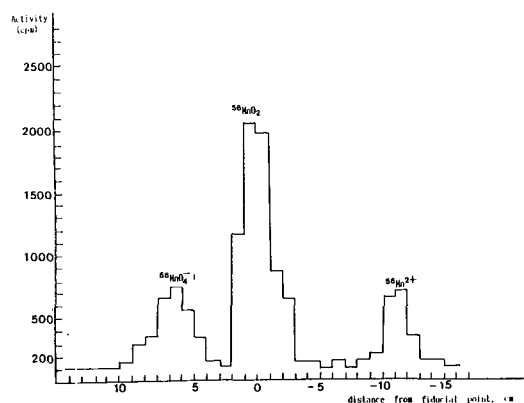
Compound	Chemical species	non-annealed	100°C one-hour-annealed	130°C one-hour-annealed
KMnO_4	A	16.1 ± 0.7	11.7 ± 0.6	14.1 ± 0.7
	B	50.3 ± 2.3	51.2 ± 1.9	43.1 ± 0.9
	C	33.6 ± 1.5	$37.1 \pm .3$	42.8 ± 1.2
NH_4MnO_4	A	10.0 ± 0.6	6.0 ± 0.3	5.4 ± 0.3
	B	54.5 ± 2.4	55.2 ± 1.9	50.4 ± 2.1
	C	35.5 ± 1.2	38.8 ± 1.5	44.2 ± 1.7
$\text{Ba}(\text{MnO}_4)_2$	A	31.4 ± 2.0	27.8 ± 1.1	21.3 ± 1.2
	B	39.2 ± 1.3	40.1 ± 1.6	38.4 ± 1.3
	C	29.4 ± 0.9	32.1 ± 0.8	40.3 ± 1.5

(A: $^{56}\text{Mn}^{2+}$, B: $^{56}\text{MnO}_2$, C: $^{56}\text{MnO}_4^-$)**Fig. 5. Annealing Curves for ^{56}Mn Recoils in Neutron Irradiated KMnO_4 , NH_4MnO_4 and $\text{Ba}(\text{MnO}_4)_2$**

tively.

Discussion

The yield of MnO_4^- at low pH and high pH could be explained by following terms.⁹⁾

**Fig. 6. Paper-Electrophoresis Histogram of Neutron-Irradiated NH_4MnO_4**

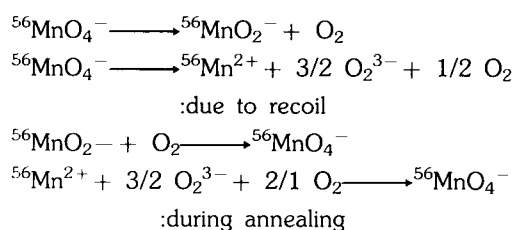
1. Low pH: oxygen exchange predominates.
 $\text{Mn}^*\text{O}_3^+ + \text{MnO}_4^- \rightleftharpoons \text{Mn}^*\text{O}_4^- + \text{MnO}_3^+$
2. high pH: hydration by OH^- predominates.
 $\text{MnO}_3^+ + \text{OH}^- = \text{H}^+ + \text{MnO}_4^-$
3. Intermediate pH: reduction by H_2O predominates.



The higher retention values in kaolinite ($4\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$) and alumina (Al_2O_3) are probably due to the presence of aluminium oxide, that is, the increase in recombination events results from Mn^{2+} recoils that escape from capture

on the alumina surface. The low retention in zeolite A-3 ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$) is probably due to the reaction of Mn^{2+} recoils with sodium oxide.

In hot zone, chemical reaction, returning into parent form, in the quenched hot zone of solid proceeds further by receiving the energy through thermal annealing. The annealing mechanism is as follow.



${}^{56}\text{MnO}_2$ and ${}^{56}\text{Mn}^{2+}$ are formed during activation and remain trapped at the recoil site. This species oxidizes to ${}^{56}\text{MnO}_4$ by second reaction on heating.

References

1. L. Szilard and T. A. Chalmers, *Nature*, 134, 462 (1934).
2. G. Harbottle and N. J. Sutin, *J. Phys. Chem.*, 62, 1344 (1958).
3. S. P. Mishra and J. Singh, *J. Radioanal. Nucl. Chem.*, 103(4), 241 (1986).
4. C. W. Owens and W. C. Lecington, *J. Inorg. Nucl. Chem.*, 35, 685 (1973).
5. M. T. A. Teeling, A. H. W. Aten, P. W. F. Louwrier, J. boersma and D. J. Apers, *J. Inorg. Nucl. chem.*, 43, 3047 (1981).
6. D. Bhatta, S. R. Monanty and K. C. Samantary, *Radiochim. Acta*, 28, 13 (1981).
7. W. F. Libby, J. Amer, *Chem. Soc.*, 62, 1930 (1940).
8. G. Van Herk Jr. and A. H. W. Aten Jr., *Radiochim. Acta*, 17, 214 (1972).
9. G. Harbottle and A. G. Maddock (Eds.), "chemical Effects of Nuclear Transformations in Inorganic Systems", North-Holland, Amsterdam, p. 123 (1979).