

Production and separation of manganese-54 from alpha-irradiated V₂O₅ target

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Abstract Our aim was to obtain and isolate the carrier-free gamma emitter, ⁵⁴Mn. Manganese-54 was produced via cyclotron activation in the ⁵¹V(α,n)⁵⁴Mn reaction, and separated from HCl solution on Dowex-50 × 8 resin. The effectiveness of chemical separation was checked using the internal tracer ⁴⁸V, produced in a cyclotron via the ^{nat}Ti(p,xn)⁴⁸V reaction. The microcomponent ⁵⁴Mn was eluted from the column with 3 M HCl, and vanadium with a 0.1 M HCl/ethanol/H₂O₂ mixture. The pair Ti/⁴⁸V was separated on Dowex-50 × 8, using 0.03 M HClO₄ as the eluent for ⁴⁸V and 1 M HClO₄ for ^{nat}Ti. The carrier-free ⁵⁴Mn was of 99.9% radionuclide purity. In separation of the carrier-free pair ⁵⁴Mn/⁴⁸V, the recovery yield was 98.7% for ⁵⁴Mn and 96.4% for ⁴⁸V.

Key words ion-exchange chromatography • isotope production • cyclotron • ⁵⁴Mn • ⁴⁸V

Introduction

Manganese as Mn⁺², Mn⁺³ and Mn⁺⁴ ions is involved in the metabolism of proteins, lipids and carbohydrates, and serves as cofactor for enzymes such as decarboxylase, hydrolase and kinase. Manganese ions are localized in mitochondria. Manganese is known to be an essential microelement for the development and functioning of the brain. The isotope ⁵⁴Mn is used as ⁵⁴MnCl₂ in preclinical research for understanding the function and the movement in the brain [2, 11, 12].

Moreover, as manganese exists in relatively large amounts in soil and groundwater, it can serve as a tracer in environmental monitoring. Due to its long half-life and single, high intensity gamma emission line, ⁵⁴Mn is an excellent calibration source.

The aim of our work was to obtain radioisotopically pure, carrier-free ⁵⁴Mn for further possible applications. The cyclotron AIC-144 operating in our Institute gave us the opportunity to produce it by alpha-particle activation, in the ⁵¹V(α,n)⁵⁴Mn reaction. The cross section of this reaction is 0.35076 b at 20 MeV [3], and the cross section of the competing reaction ⁵¹V(α,p)⁵⁴Cr, estimated from the lower energy data [7] is about three orders of magnitude lower. This allowed us to expect that we can obtain a product of high radionuclide purity. We have not considered alternative production ways, ⁵⁴Fe(n,p)⁵⁴Mn [10] or ⁵⁸Ni(n,αp+αp)⁵⁴Mn [5] because we had no access to the fast neutron reactor. To separate the radioactive product from the target we chose ion-exchange chromatography. To observe directly the separation processes, we used semi-quantitative colorimetric methods, and for accurate control of the effectiveness

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Table 1. Nuclear properties of ^{54}Mn and ^{48}V

Isotope	$T_{1/2}$	Decay mode	Gamma emissions	
			Energy [keV]	Intensity [%]
^{54}Mn	312.3 d	EC (100%)	834.80	99.98
		β^- (< 2.9E-4)	–	–
^{48}V	15.9735 d	EC+ β^+ (100%)	802.87	0.15
			928.29	0.77
			938.00	0.0008
			944.13	7.76
			983.52	99.98
			1063.19	0.005
			1312.10	97.60
			1437.48	0.12
			2240.38	2.41
			2375.21	0.01
			2420.90	0.01
			511.00	2×49.9

of separation we prepared the carrier-free internal tracer ^{48}V . The versatility of the AIC-144 cyclotron allowed us to produce it on the spot, in the proton induced $^{nat}\text{Ti}(p,xn)^{48}\text{V}$ reaction. This tracer was separated from the target also by ion-exchange chromatography. The nuclear properties of the isotopes used in this study are listed in Table 1.

We were expecting some difficulties in chemical separation procedures because it is well known that in water solutions, vanadium can exist in many oxidation states, in the form of oxyanions as well as oxycations [1, 9]. In this work, we were trying to develop a method which could let us to separate our main radioactive product ^{54}Mn , without special care for oxidation states of the target material. Similarly, in separation of the tracer ^{48}V from its production target, titanium, our aim was to separate carrier-free ^{48}V quantitatively, independently of its chemical form or oxidation state. To do this, we performed procedures which are described in further paragraphs.

Experimental

Target preparation and irradiations for ^{54}Mn

The target for production of ^{54}Mn in the $^{51}\text{V}(\alpha,n)^{54}\text{Mn}$ nuclear reaction was prepared from high purity V_2O_5 (Spectrographically Standardised Substance, Johnson, UK). Portion of about 80 mg V_2O_5 was formed in a pellet, fixed on an indirectly cooled aluminium support and covered with an aluminium foil ($2 \text{ mg}\cdot\text{cm}^{-2}$ Al). Afterwards, the target was bombarded during 5 h with an internal beam of alpha particles in the AIC-144 cyclotron at our Institute. The beam current was $1 \mu\text{A}$, and the incident alpha energy was 20 MeV.

Production of the ^{48}V tracer

The isotope ^{48}V was obtained in the nuclear reaction $^{nat}\text{Ti}(p,xn)^{48}\text{V}$, also carried out at the AIC-144 cyclotron.

The targets were prepared from high purity TiO_2 (Reachim, former USSR) or from the rutile-form of TiO_2 (particle size: 23 nm, brand name: R-HD2, Huntsman, Germany). Portions of about 100 mg TiO_2 were formed in pellets, covered with the aluminium foil ($2 \text{ mg}\cdot\text{cm}^{-2}$ Al), and fixed on the indirectly cooled aluminium support. Afterwards, the target was bombarded during 3 h with the internal proton beam of the AIC-144 cyclotron. The beam current was $1.5 \mu\text{A}$, and the incident proton energy was 20 MeV.

Radioactive measurements

All radioactive products were identified by gamma-ray spectrometry. The spectra were recorded using an HPGe co-axial detector (35 cm^3 , IFJ, Cracow, Poland) coupled with a multichannel analyser (Silena, Milano, Italy) and processed with the EMCAPLUS program (Silena, Milano, Italy). Activity of each radioactive solution before and after chemical separation was measured also on a Radiometer RUM-1 with the scintillation probe SSU-3-2 (all from Polon-Alfa, Bydgoszcz, Poland).

Dissolution of V_2O_5 target

The irradiated target (80 mg) was dissolved in 2 ml of 1 M HCl. The mixture was heated for 15 min at 80°C until complete dissolution of the sample. A yellow product which was thus obtained was later evaporated to dryness. The dry residue was re-dissolved in 2 ml of 0.1 M HCl.

Dissolution of TiO_2 targets

The irradiated TiO_2 target (100 mg) was dissolved in 4 ml of concentrated H_2SO_4 (98%) in the presence of 1.6 g $(\text{NH}_4)_2\text{SO}_4$ [8]. The mixture was heated for 2 h at $250\text{--}260^\circ\text{C}$ to complete dissolution of the sample. Then, in order to get rid of SO_4^{2-} 2 ml of 20% $\text{Pb}(\text{NO}_3)_2$ were added to the solution. After centrifugation, the solution was separated from the precipitate of PbSO_4 and washed out with water. Afterwards, both phases were analyzed with the germanium detector, in order to obtain information about the radioactive products. The aqueous phase from the first separation was evaporated to dryness during 6 h at 150°C on a sandbath. The dry residue, a yellow product, was re-dissolved in 1.5 ml of 0.5 M HClO_4 .

Preparation of columns

A portion of Dowex-50 \times 8/100 mesh resin was soaked in 0.1 M HCl during 24 h, and then it was transferred onto columns. Two different columns were prepared for the purpose. Parameters of column 1 were: diameter = 0.3 cm, h = 10 cm, free volume = 0.5 ml, $V_{\text{resin}} = 0.7065 \text{ cm}^3$. Parameters of column 2 were: diameter = 0.5 cm, h = 20.5 cm, free volume = 2 ml, and $V_{\text{resin}} = 4.023 \text{ cm}^3$. Just before use, the ion-exchange columns were washed with deionised water.

Separation of ⁵⁴Mn from target material (V₂O₅)

Firstly, column 1 was prewashed with 10 ml of 0.1 M HCl and afterwards 2 ml of a mixture of ⁵⁴Mn and stable vanadium in 0.1 M HCl was placed on it. The macro-component, vanadium was eluted from the column with a 0.1 M HCl + ethanol (5:1 v/v) mixture doped with a few drops of 3% H₂O₂, and manganese ⁵⁴Mn was eluted later with 3 M HCl. A total of 30 fractions, each of 0.5 ml, was collected. The fractions from 23 to 26 were used for further experiments.

Separation of ⁴⁸V from target material (TiO₂)

After dissolving TiO₂ and removing the excess of SO₄²⁻ ions, we exactly followed the procedure developed in our laboratory many years ago [6].

Colorimetric detection of vanadium

In order to detect vanadium in the eluate, one drop of the solution from each fraction from Ti/V separation was mixed with one drop of 20% H₂SO₄. After a few minutes, a drop of 1% H₂O₂ was added to the solution. According to the amount of vanadium present, a red to pink coloration was appearing. The reported limit of identification of vanadium is 2.0×10^{-3} g/dm³ [4].

Preparation of carrier-free ⁵⁴Mn and ⁴⁸V

Two portions of ⁵⁴Mn and ⁴⁸V obtained from the above separations, each dissolved in 1 ml of 1 M HCl were mixed together. The resultant solution was evaporated to dryness and then re-dissolved in 2 ml of 0.1 M HCl.

Separation of the mixture ⁵⁴Mn/⁴⁸V on the column

Ion-exchange column 2 was prewashed with 10 ml of 0.1 M HCl. As the next step, 2 ml of the solution containing of 6.85 kBq ⁵⁴Mn and 8.01 kBq ⁴⁸V were placed on the column. Under the above conditions, vanadium was leaving the column first, with 0.1 M HCl

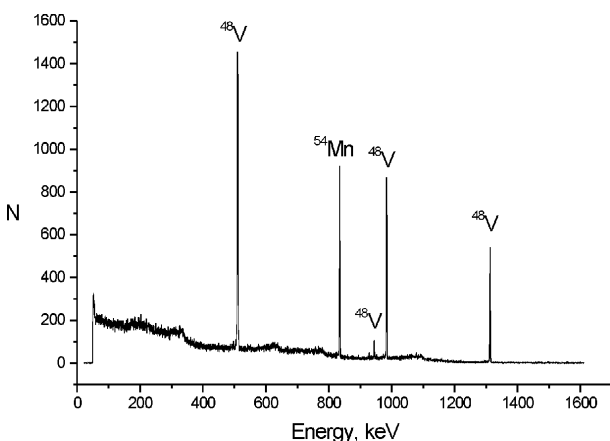


Fig. 1. Gamma spectrum of the mixture ⁵⁴Mn/⁴⁸V.

+ ethanol (5:1 v/v) to which few drops of 3% H₂O₂ were added, and manganese ⁵⁴Mn was eluted later with 3 M HCl. There were 35 fractions of eluate, each of 1 ml.

Control of radionuclide purity

The fractions from 3 to 18 (all of them containing ⁴⁸V) were collected together in one vial, then the mixture was evaporated up to 2 ml. The same was done with the fractions from 22 to 35, containing ⁵⁴Mn. Afterwards, each vial was analyzed by means of gamma-ray spectrometry, with the germanium detector.

Results

Separation of the ⁵⁴Mn/⁴⁸V pair

The gamma spectrum of the mixture of the isotopes ⁵⁴Mn/⁴⁸V before being put on the ion-exchange column is shown in Fig. 1.

Figure 2 presents the distribution of ⁴⁸V and ⁵⁴Mn activities between various fractions of the eluate. It can be seen that the tracer ⁴⁸V was eluted from the column as several different species and ⁵⁴Mn in only one chemical form.

Figure 3 shows the gamma spectrum of the sum of the fractions 22 to 35 of the eluate. Apart from the sharp

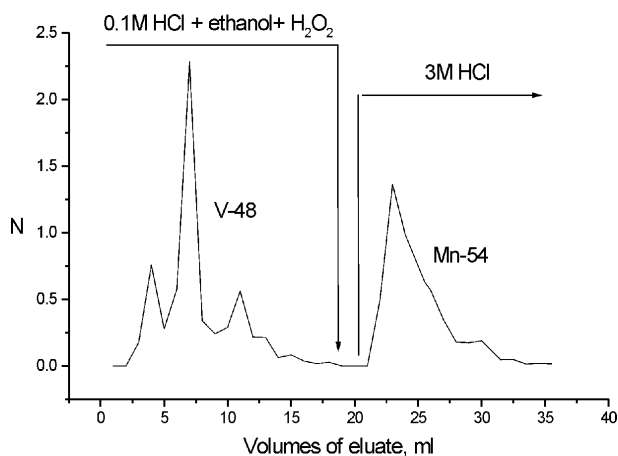


Fig. 2. Separation of the mixture ⁵⁴Mn/⁴⁸V.

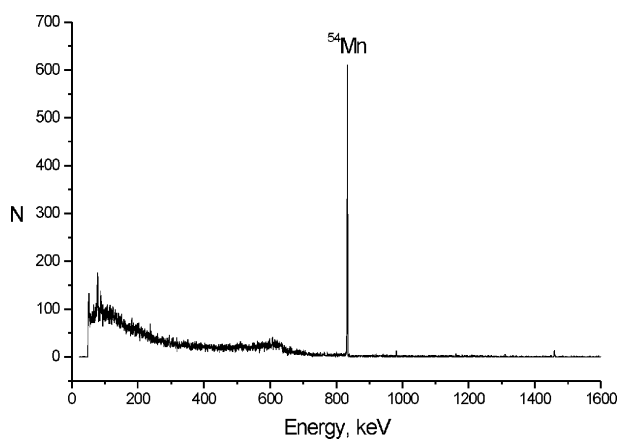


Fig. 3. Gamma spectrum of ⁵⁴Mn.

Table 2. Recovery of ^{54}Mn and ^{48}V . Second column: both tracers in carrier-free form. Third column: ^{54}Mn carrier free, ^{48}V in the presence of bulk target material

Isotope	Mn/V micro/micro	Mn/V micro/macro
^{54}Mn	$98.7 \pm 6.3\%$	$95.2 \pm 3.6\%$
^{48}V	$96.4 \pm 2.4\%$	$92.2 \pm 3.3\%$

^{54}Mn peak and the normally observed background peaks (especially the 1460 keV peak of natural ^{40}K) no other gamma activity was observed. Similarly, no activity of ^{54}Mn was observed in the sum of the fractions 1 to 21. The obtained data indicate that radionuclide purity of the separated ^{54}Mn was higher than 99.9%.

The recovery yield of ^{54}Mn and ^{48}V was calculated as $A_1/A_0 \times 100$, where A_0 is the initial activity of the isotope, and A_1 is the total activity of the same isotope in the eluate (corrected for decay). It was found that the corresponding values were 98.7% for ^{54}Mn and 96.4% for ^{48}V (Table 2).

Separation of the $^{48}\text{V}/\text{Ti}$ pair

Our radiometric measurements confirmed the earlier observations that the separation method with HClO_4 as the eluent gives ^{48}V of high radionuclide purity.

Discussion

The main purpose of this work was the separation of carrier-free ^{54}Mn from vanadium target. However, knowing that in aqueous solutions vanadium may exist in a variety of chemical forms, we could expect that this might influence the effectiveness of separation.

Indeed, we have demonstrated in practice that the chemical form of vanadium is important, because in the conditions described above vanadium is leaving the column first. If, due to the variety of chemical forms, the elution curve of vanadium is broadened, the first fractions of ^{54}Mn may be contaminated with the target material.

We have observed the most pronounced broadening when vanadium was eluted with HCl only (without the oxidant), moreover, we could see that in such systems vanadium was not completely eluted from the column. The addition of H_2O_2 to the eluent improves the separation significantly, and the best conditions for the recovery of vanadium from the ion-exchange column took place when the elution with 0.1 M HCl was carried out in the presence of 3 drops of 3% H_2O_2 per 10 ml. Under these conditions, vanadium is converted to its upper oxidation state, but, as it is shown in Fig. 2, even in such cases we observed several elution peaks, apparently due to the corresponding number of chemical forms of vanadium in water solution. As it was shown by our radiometric measurements, in $^{54}\text{Mn}/^{48}\text{V}$ separation, all these forms were eluted from the column quantitatively, no matter whether vanadium was present as a macrocomponent (target material) or as a microcomponent (carrier-free ^{48}V tracer, separated from Ti).

In case of manganese, it is known that its most stable oxidation state is +2 [1], even in the acidic medium and in the presence of H_2O_2 . The shape of our elution curves confirms this feature: ^{54}Mn was separated as a single chemical form.

The visual control of separation was a great help during this work, because natural changes of color let us to observe all processes currently. However, for quantitative evaluation such a simple "colorimetric" method is not sensitive enough, and this is why we decided to use the isotope ^{48}V as an internal tracer of ^{54}Mn purification.

Conclusions

Under the conditions described above, the carrier-free isotope ^{54}Mn was obtained and separated, as planned.

The resultant ^{54}Mn was of high radionuclide purity and did not contain detectable traces of the target material (Fig. 3).

The method for the production and separation of carrier-free ^{48}V tracer from TiO_2 turned out to be efficient but rather cumbersome because of low solubility of TiO_2 whose dissolution required drastic conditions.

References

1. Bielański A (1998) Principles of inorganic chemistry. Part 3, 3rd ed. PWN, Warsaw (in Polish)
2. Chauncey Jr DM, Schelbert HR, Halpern SE *et al.* (1977) Tissue distribution studies with radioactive manganese: a potential agent for myocardial imaging. *J Nucl Med* 18;9:933–936
3. Chowdhury DP, Sujit Pal, Saha SK, Gangadharan S (1995) Determination of cross section of α -induced nuclear reaction on natural Cr and Zr by stacked foil activation for thin-layer activation analysis. *Nucl Instrum Methods Phys Res B* 103;3:261–266
4. Feigl F, Anger V (1972) Spot tests in inorganic analysis, 6th ed. Elsevier, Amsterdam–London–New York
5. Fessler A, Qaim SM (1999) Excitation functions of $^{50}\text{Cr}(n, np + pn + d)^{49}\text{V}$, $^{58}\text{Ni}(n, \alpha)^{55}\text{Fe}$, $^{58}\text{Ni}(n, \alpha p + p\alpha)^{54}\text{Mn}$ and $^{62}\text{Ni}(n, \alpha)^{59}\text{Fe}$ reactions. *Radiochim Acta* 84:1–10
6. Grychowski P, Petelenz BU, Mikulski J (1985) Separation of vanadium-48 from deuteron-irradiated TiO_2 target. *J Radioanal Nucl Chem* 89:123–130
7. Hansper V, Morton A, Tims S, Tingwell C, Scott A, Sargood DG (1993) Cross section and thermonuclear reaction rates for $^{51}\text{V}(\alpha, n)^{54}\text{Mn}$ and $^{51}\text{V}(\alpha, p)^{54}\text{Cr}$. *Nucl Phys A* 551;1:158–172
8. Korn MA, Ferreira AC, Costa ACS, Nobrega JA, Silva CR (2004) Comparison of decomposition procedures for analysis of titanium dioxide using inductively coupled plasma optical emission spectrometry. *Microchem J* 71:41–48
9. Pyrzyńska K, Wierzbicki T (2004) Determination of vanadium species in environmental samples. *Talanta* 64:823–829
10. Saeed MM, Rusheed A (1999) Production of no carrier-added Mn-54 using HTTA-loaded polyurethane foam. *Radiochim Acta* 84;1:1–10
11. Takeda A (2003) Manganese action in brain function. *Brain Res Rev* 41;1:79–87
12. Takeda A, Ishwatorai S, Okada S (1998) *In-vivo* simulation – induced release of manganese in rat amygdala. *Brain Res* 811:147–151