Separation of No-Carrier-Added ^{52}Mn from Bulk Chromium: A Simulation Study for Accelerator Mass Spectrometry Measurement of ^{53}Mn

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^{53}Mn radionuclide ($T_{1/2} = 3.7 \times 10^6$ y) is produced through the interaction of cosmic rays. Measurements of concentrations of ^{53}Mn in rocks might help to understand Earth surface processes that occurred in time periods not accessible with other cosmogenic nuclides. Only accelerator mass spectrometry (AMS) can determine such ultratrace levels of ^{53}Mn. The main interference in the detection of ^{53}Mn by AMS is its stable isobar ^{53}Cr, which is roughly $\sim 10^{12}$ times more abundant in nature. A prerequisite of any AMS measurement of ^{53}Mn in geological samples is therefore chromium separation by an efficient chemistry. Thus, we have developed a method for the separation of chromium and manganese by using a radiometric simulation. The separation procedure was monitored by ^{51}Cr ($T_{1/2} = 27.70$ d) and ^{52}Mn ($T_{1/2} = 5.59$ d) as the corresponding radiotracers for chromium and manganese, respectively. The separation studies were performed by a liquid−liquid extraction technique using trioctylamine (TOA) diluted in cyclohexane. A high separation factor ($\sim 16\,000$) for Mn and Cr can be obtained at optimal conditions of 0.8 M TOA and 9 M HCl. The developed method has been found equally applicable for real geological samples such as manganese crusts, lava, and sediment samples. Therefore, the method offers an important tool to improve ^{53}Mn measurements by AMS.

^{53}Mn ($T_{1/2} = 3.74 \times 10^6$ y) in Earth surface samples is dominantly produced by nuclear reactions on iron present in surface minerals. The amounts of ^{53}Mn, measurable in the samples, might reveal Earth's surface processes that occurred during a few half-lives of ^{53}Mn. It potentially combines several advantages such as the following: (i) production rates have a very simple dependence on rock composition—iron is the only major target element; (ii) ^{53}Mn concentrations in rocks record events that occurred in time periods not readily accessible with other cosmogenic nuclides.

The abundance of ^{53}Mn in the Earth's crust is scanty and might be in the ratio of ^{53}Mn/^{55}Mn $\sim 1/1 \times 10^{14}$, depending on the location. Recent advances have made it possible to measure ^{53}Mn

produced in rocks at the Earth's surface by using accelerator mass spectrometry (AMS).[1] However, the main interference in the detection of ^{53}Mn by AMS is its stable isobar ^{53}Cr, which is $\sim 10^{12}$ times more abundant in natural samples such as manganese crust, sediment, or lava samples. Thus, it is important to develop a chemical method to separate manganese from the much larger amount of chromium. Therefore, a study has been undertaken to simulate the condition where a particular isotope of manganese will be in scanty amounts but chromium will be in much larger amounts, a situation near to the abundance ratio of ^{53}Mn and ^{53}Cr in Earth's surface. The ratio of ^{52}Mn/Cr produced by the nuclear reaction ^{nat}Cr(p,xn)^{52}Mn will be similar to this.

In an earlier experiment, no-carrier-added ^{52,56}Mn radionuclides were produced by α-particle irradiation on an iron target. Mn along with other activation products was separated from bulk iron by extracting iron with diethyl ether and 6 M HCl.[2] ^{57}Mn, produced in an iron target,[3,4] was separated through precipitation as MnO_2 by the addition of $KClO_3$ under boiling conditions. No-carrier-added ^{52,54}Mn radionuclides were produced by α-particle irradiation on Cr_2O_3 target by Lahiri et al.[5] The target matrix Cr_2O_3 was treated with aqua regia, boiled, and filtered. The filtrate contained only ^{52,54}Mn radionuclides. The efficiency of Mn separation using this method was very low, as most of the Mn remained in the target matrix and only a fraction of Mn could be recovered. Klein et al.[6] produced no-carrier-added ^{51}Mn by the reaction of a very high current deuteron beam on an enriched $^{50}Cr_2O_3$ target. Several techniques such as cation and anion exchange chromatography, solid-phase extraction, liquid−liquid extraction (LLX) using acetic acid in $CHCl_3$ as extracting agent, and coprecipitation of radioactive manganese along with $Fe(OH)_3$ were employed.
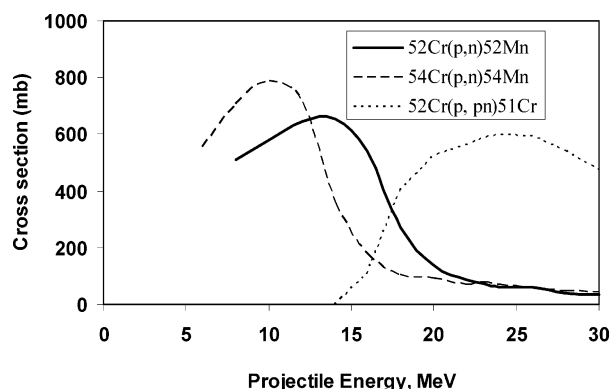
In the present work, we have developed a method to separate no-carrier-added ^{52}Mn (ultratrace level) from bulk chromium. ^{52}Mn was produced through the ^{52}Cr(p, n)^{52}Mn reaction; while ^{51}Cr was

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Figure 1. Theoretical production cross sections for various radio-nuclides produced by proton irradiation on chromium target (calculated from ALICE code).

produced by the $^{52}Cr(p, pn)^{51}Cr$ reaction. ^{54}Mn was also copro-duced through the $^{54}Cr(p, n)^{54}Mn$ reaction. An attempt has also been made to verify the efficacy of the developed method with three real geological samples collected from different locations.

EXPERIMENTAL SECTION

A. Separation of No-Carrier-Added ^{52}Mn from Different Proton Irradiated Chromium Targets. Irradiation. Four types of chromium targets were irradiated with a proton beam. (i) A chromium metal target of thickness 1 mg/cm² and 1-cm diameter was prepared by an evaporation technique from flakes of pure Cr metal. In a geological sample, such as samples from sediments, rocks, or lava, Cr is present not only in Cr(III) form but may also be present as anionic Cr(VI) [$Cr_2O_7^{2-}$]. Therefore, the other three targets were (ii) $Cr(NO_3)_3 \cdot 9H_2O$, (iii) $K_2Cr_2O_7$, and (iv) mixture of $Cr(NO_3)_3 \cdot 9H_2O$ and $K_2Cr_2O_7$ salts of equal amounts. Pellets of 1-cm diameter each were prepared by pressing ∼ 43 mg of the corresponding salts; the thickness of each targets were ∼54.6 mg cm^{-2}. An HPGe detector of 2.13-keV resolution at 1.33 MeV in conjunction with a PC-based MCA, PCA2 (Oxford) was used for γ-spectrometric studies.

To get maximum activity, the projectile energy was determined by calculating excitation functions of different nuclear reactions using a statistical model code ALICE-91[7] (Figure 1). From the calculation, it is clear that the maximum cross sections for the $^{52}Cr(p,n)^{52}Mn$ and $^{52}Cr(p,pn)^{51}Cr$ reactions are at 12 and 24 MeV, respectively. Because of technical reasons, we have irradiated all the chromium samples described above with both 12- and 23-MeV energy with a 1-cm collimated proton beam at the BARC-TIFR Pelletron (Mumbai, India). The average beam current was 500 nA, and irradiation time was 5 h for each sample at each of the projectile energy. Along with ^{52}Mn, some amount of ^{54}Mn (312.1 d) will also be produced in the matrix. However, because of the longer half-life and the low natural abundance of the target isotope of only 2.4% (^{54}Cr), the activity of ^{54}Mn will be much less compared to ^{52}Mn. Therefore ^{52}Mn has been chosen to be representative of Mn throughout the experiment.

Chemical Procedure. The liquid anion exchanger, triocty-lamine (TOA), was purchased from E. Merck. The extracting solutions of the desired concentrations (0.1−0.8 M) were prepared

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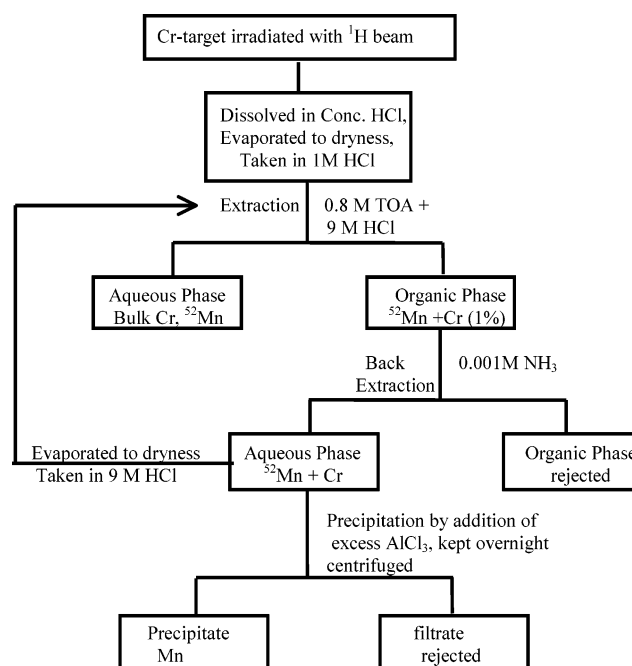
Figure 2. Schematic diagram for the separation of no-carrier-added ^{52}Mn from the Cr target.

by adding calculated amounts of TOA to cyclohexane. After measuring the γ spectra, all the Cr targets were dissolved separately in concentrated HCl, evaporated to dryness, and taken in 1 (for Cr metal) and 4 mL (for all other salts) volume in 1 M HCl medium. The concentration of chromium in the stock solution for chromium metal, $Cr(NO_3)_3 \cdot 9H_2O$, $K_2Cr_2O_7$, and a mixture of $Cr(NO_3)_3 \cdot 9H_2O$ and $K_2Cr_2O_7$ were 0.78, 1.4, 3.8, and 2.6 mg/mL, respectively.
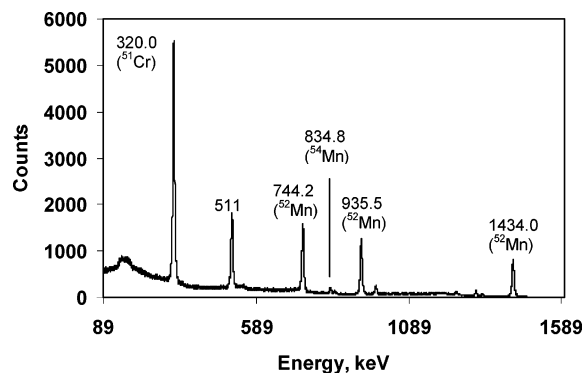
To study the separation and extraction profile, 200 μL of each of the active stock solutions was taken in a 10-mL HCl solution of varying strengths between 1 and 10 M HCl and the solution was shaken vigorously with an equal volume of TOA, for ∼5 min. After separation of the liquid phases, the activities present in both the liquid phases were again measured by γ-ray spectrometry. As ^{52}Mn is extracted in organic phase, it is back extracted into the aqueous phase by shaking with 0.001 M NH_3. Excess $AlCl_3$ was added to aqueous solution to precipitate $Mn(OH)_2$ along with $Al(OH)_3$.

A summary of the chemical procedure developed for the separation of ^{52}Mn from irradiated Cr is schematically presented in Figure 2.

B. Verification of the Developed Method for Separation of Mn from Cr in Geological Samples. Sample Origin. Three geological samples from different locations have been tested. 83MC is a sediment sample collected from the Pacific, TOF 52 is a lava sample from the South pacific, near Tonga islands, and SO65 is a manganese crust originating from the South Pacific.

Dissolution of the Samples and Chemical Procedure. A 43-mg aliquot of the 83MC sample was mixed with 0.5 mL of proton-irradiated $Cr(NO_3)_3$ solution in HCl containing a known amount of ^{51}Cr and ^{52}Mn activity. The mixture was treated with 2 mL of concentrated HCl and 1 mL of concentrated HNO_3, evaporated to dryness, the process repeated twice, then dissolved in 2 mL of 9 M HCl, evaporated to dryness twice, and finally taken in 2 mL of 9 M HCl solution, which was treated as stock solution for 83MC. Similarly, 43.6 mg of SO65 was spiked with ^{51}Cr and

Figure 3. γ Spectrum of the proton-irradiated Cr target showing both ^{52}Mn and ^{51}Cr.

Figure 4. (a) Extraction profiles of no-carrier-added ^{52}Mn and bulk Cr with varying concentrations of HCl and 0.5 M TOA in cyclohexane with 0.025 mL of octanol (pure Cr metal target). (b) Extraction profiles of no-carrier-added ^{52}Mn and bulk Cr with varying concentrations of TOA in cyclohexane and 8 M HCl with 0.025 mL of octanol (pure Cr metal target).

^{52}Mn and dissolved following the same method. However, TOF samples cannot be dissolved in the same way. Therefore, the 43.6 mg of TOF sample was taken in a plastic beaker and mixed with a 0.5-mL proton-irradiated $Cr(NO_3)_3$ solution in HCl containing a known amount of ^{51}Cr and ^{52}Mn activity. The mixture was treated with 2 mL of concentrated HF and 1 mL of concentrated HNO_3, evaporated to dryness with the help of a water bath, repeated twice, dissolved in 2 mL of concentrated HCl and 1 mL of concentrated HNO_3, evaporated to dryness, repeated twice, and finally taken in 2 mL of 9 M HCl, which was treated as stock solution for TOF.

A 0.5-mL aliquot of each stock sample from the corresponding geological samples was taken in 3 mL of 9 M HCl, mixed with 3 mL of 0.8 M TOA dissolved in cyclohexane and 0.025 mL of octanol. The mixture was shaken for 10 min in a mechanical shaker and settled for another 10 min. The organic phase containing Mn was back extracted to the aqueous phase by 1 M NH_3. The extraction back extraction cycle was repeated twice. Excess $AlCl_3$ was added to aqueous phase for coprecipitation of $Mn(OH)_2$ alongside with $Al(OH)_3$.

RESULTS AND DISCUSSION

A. Separation of No-Carrier-Added ^{52}Mn from Different Proton-Irradiated Chromium Targets. The γ spectrum (Figure 3) of the proton-activated Cr target, before the chemical separation, shows the presence of ^{51}Cr and ^{52,54}Mn in the matrix as concluded from the theoretical calculation of the excitation function stated above. The nuclear reactions for the production of ^{51}Cr and ^{52,54}Mn are as follows:

$$^{52}Cr\ (83.8\%)\ (p,n)\,^{52}Mn\ (5.61\ d) \quad (E_p = 12\ MeV)$$

$$(p,pn)\,^{51}Cr\ (27.7\ d) \quad (E_p = 23\ MeV)$$

$$^{54}Cr\ (2.4\%)\ (p,n)\,^{54}Mn\ (312.1\ d) \quad (E_p = 12\ MeV)$$
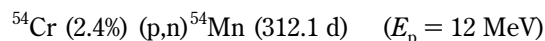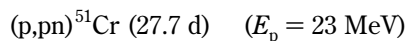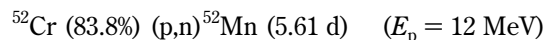
To separate Mn and Cr, liquid–liquid extractions were carried out with TOA in cyclohexane from HCl solutions of different strength. Figure 4a shows the extraction profile of bulk Cr and the no-carrier-added ^{52}Mn produced by the irradiation of the pure Cr metal target. The concentration of the organic phase was kept constant at 0.5 M TOA. It has been observed that, from 1 to 9 M HCl concentrations, the extractability of Mn increases with
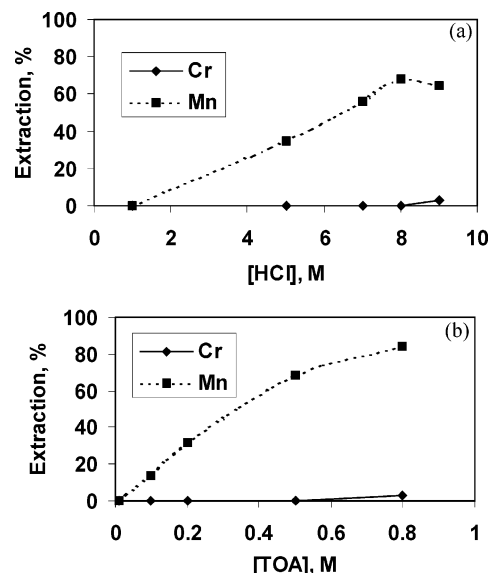
increasing acid strength with a maximum at 8 M HCl. On the other hand, Cr remains completely in the aqueous solution up to 8 M HCl concentration. Therefore, to get the optimal condition, the concentration of TOA was varied, keeping HCl concentration fixed at 8 M. Figure 4b shows that the extractability of ^{52}Mn increases with the TOA concentration. As in higher TOA concentrations, third phase formation was observed; in each extraction 0.025 mL of octanol was added to suppress the third phase.[8,9] At 0.8 M TOA concentration, Mn was extracted 85% in the organic phase keeping Cr in the aqueous phase. The high extractability of no-carrier-added ^{52}Mn radionuclide in HCl medium might be explained by the formation of $[MnCl_4]^{2-}$, which in turn is extracted by the anionic extractant TOA.[10] It is noteworthy to mention that at 1 M TOA concentration and above the volume of third phase increases rapidly and the amount of octanol necessary to suppress the third phase is much higher than 0.025 mL. As octanol has a pronounced antagonistic effect on the extraction of metal ions, it lowers the extraction of both Mn and Cr, and hence throughout the experiment, 0.8 M TOA has been used as optimum TOA concentration.

Liquid–liquid extraction studies with a mixture of chromium salts were carried out with the TOA–HCl system. The LLX data presented above show that 0.8 M TOA concentration is the optimum reagent concentration for maximum extraction of ^{52}Mn with minimum chromium contamination (Figure 4b). In the mixed sample to get the optimum condition, the concentration of HCl was varied while keeping the reagent concentration fixed at 0.8 M TOA (Figure 5a). The pattern of the extraction profile of both

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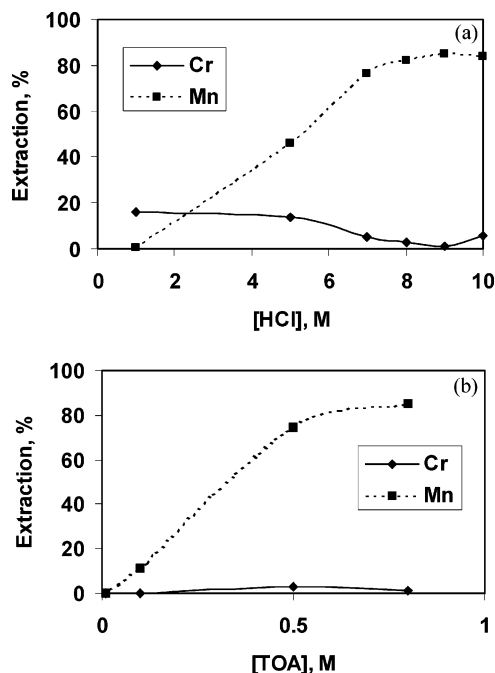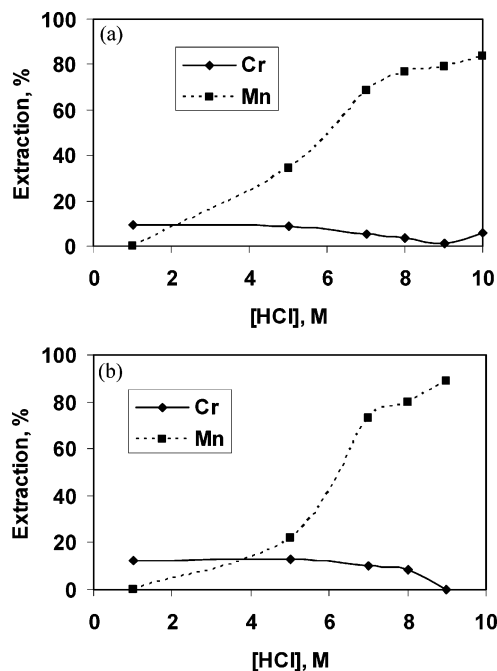
Figure 5. (a) Extraction profiles of no-carrier-added ^{52}Mn and bulk Cr with varying concentrations of HCl and 0.8M TOA in cyclohexane with 0.025 mL of octanol (mixture of $Cr_2O_7^{2-}$ & Cr^{3+} target). (b) Extraction profiles of no-carrier-added ^{52}Mn and bulk Cr with varying concentrations of TOA in cyclohexane and 9 M HCl with 0.025 mL of octanol (mixture of $Cr_2O_7^{2-}$ and Cr^{3+} target).

Cr and Mn was found similar to that of Figure 4a, although some minor extraction of Cr was found at lower acid concentration. A significant extraction (85%) of ^{52}Mn was found at 9 M HCl. Figure 5b represents the extraction of ^{52}Mn and bulk Cr at 9 M HCl with varying TOA concentration. Similarly, panels a and b in Figure 6 represent the extraction profile of Cr and Mn in proton-irradiated $Cr(NO_3)$ and $K_2Cr_2O_7$, respectively. In both cases, the HCl concentration was varied while keeping 0.8 M TOA concentration fixed. It is evident from all six panels (Figures 4a, b, 5a, b, and 6a, b) that the optimum condition is 9 M HCl and 0.8 M TOA, where ^{52}Mn is extracted in a significant amount in the organic phase with maximum 1% contamination of Cr. Moreover, it is evident from the same types of extraction profile that, irrespective of their initial form, all the chromium is converted to Cr^{3+}. For example, Cr(VI) is strongly oxidizing and the redox potential is very low ($E° = 1.33$ V). All the dichromate present in the target was converted to Cr(III) by the reaction with HCl during dissolution with concentrated HCl. TOA being a liquid anion exchanger could not extract Cr(III) into the organic phase.

From the mixture target, the extracted Mn was back extracted into aqueous solution using 0.1 M HCl or 0.001 M NH_3. The ~1% contamination of Cr was removed by repeating the extraction−back extraction cycle twice. Finally, ^{52}Mn was coprecipitated as $Mn(OH)_2$ alongside $Al(OH)_3$. The precipitation efficiency (count of ^{52}Mn in the precipitate/count of ^{52}Mn in the back extracted ammonical phase) was found to be 92%. The chemical yield of ^{52}Mn (count of ^{52}Mn in the precipitate/initial count of ^{52}Mn in HCl solution) was 60%.

A separation factor of ~16 000 has been achieved at optimal conditions from the mixture target (Table 1). Figure 7 depicts the γ spectra of the Mn activity in the TOA extract at optimal

Figure 6. (a) Extraction profiles of no-carrier-added ^{52}Mn and bulk Cr with varying concentrations of HCl and 0.8 M TOA in cyclohexane with 0.025 mL of octanol ($Cr(NO_3)_3 \cdot 9H_2O$ target). (b) Extraction profiles of no-carrier-added ^{52}Mn and bulk Cr with varying concentrations of HCl and 0.8 M TOA in cyclohexane with 0.025 mL of octanol ($K_2Cr_2O_7$ target).

Table 1. Distribution Ratios[a] (D) and Separation Factor[b] (S) of Cr and Mn at Optimal Conditions

exptl condition 9 M HCl + 0.8 M TOA + 2 drops octanol	D_{Cr}	D_{Mn}	$S_{Mn/Cr}$
first extraction	0.0112 ± 0.0002	4.223 ± 0.077	377.1 ± 13.4
second extraction	3.05×10^{-4}	5.027 ± 0.125	16482 ± 410

[a] D, (count of the radionuclide in the organic phase/count of radionuclide in aqueous phase). [b] $S = D_{Mn}/D_{Cr}$.
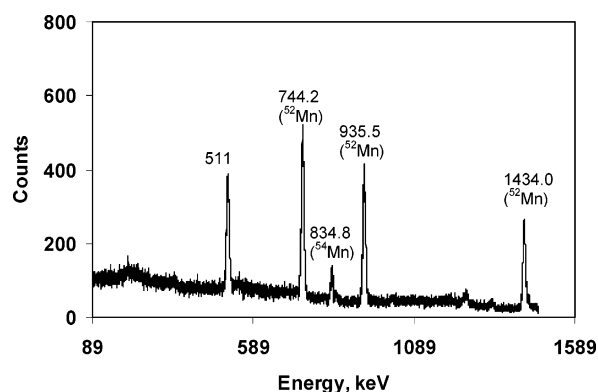
Figure 7. Expanded γ spectrum of the TOA extract showing only the peak of ^{52}Mn radionuclide.

conditions. This radiochemical separation method is an important step to separate ultratrace levels of ^{53}Mn from its stable isobar ^{53}Cr, which in turn is a prerequisite for a highly sensitive measurement of ^{53}Mn by AMS.

B. Verification of Developed Method for Separation of Mn from Cr in Geological Samples. The validity of the simulated

Table 2. Precipitation Efficiency and Chemical Yield of Mn in the Simulated and in All the Geological Samples

samples	precipitation efficiency (%)	chemical yield
simulated sample	92.0	60.0
83MC	85.2	71.6
SO65	83.2	70.6
TOF	89.7	73.0

method was checked in real geological samples with the help of the radiotracer method by spiking the geological samples with [52]Mn and ^{51}Cr followed by separation of Mn from Cr at the optimal condition described earlier.

It has been observed that the patterns of the extraction profile for all three samples were highly similar to that of the simulated samples described above. At optimum reagent concentration, i.e., at 9 M HCl and 0.8 M TOA, [52]Mn is extracted in a significant amount in the organic phase. However, in geological samples, no chromium contamination was observed at all in the organic phase. The extracted Mn was back extracted into aqueous solution using 1 M NH_3. Finally, [52]Mn was coprecipitated as $Mn(OH)_2$ alongside $Al(OH)_3$. Table 2 compares the precipitation efficiency of Mn and the overall chemical yield of Mn in all the geological samples as well as in the simulated sample.