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Further study on highly sensitive AMS measurement of ^{53}Mn

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ABSTRACT

The AMS facility at China Institute of Atomic Energy has been equipped with a ΔE-Q3D detection system for the measurements of ^{53}Mn. While the sample material of MnO_2 and the extraction ions of MnO^- were used previously in AMS measurement of ^{53}Mn with fairly good results, a method has recently been developed with the extraction of MnF^- from ion source using MnF_2 and $MnO_2 + PbF_2$ as sample materials. As a result, a sensitivity of 10^{-14} (^{53}Mn/Mn) has been achieved. Compared with the original MnO^-/MnO_2 approach, the method of MnF^- extraction, combined with ΔE-Q3D detection technique, demonstrated an improved sensitivity for AMS measurement of ^{53}Mn.

1. Introduction

The determination of cosmogenic ^{53}Mn in terrestrial formations has many interesting applications in many scientific areas. Examples are: (i) the study on the possible existence in iron meteorites and the use as a monitor of Earth surface processes; (ii) the measurement of depth profiles in deep sea ferromanganese crusts for dating on rather long time scales; (iii) measurement of erosion rates over an exposure time scale of millions of years due to its long half life of 3.7 Ma and (iv) dating over tens of million years, well beyond the upper limit of ^{10}Be/^{26}Al dating. However, the potential of ^{53}Mn dating has not been fully tapped for many years, due to the lack of appropriate method for the determination of ultra-trace ^{53}Mn.

In recent years, two kinds of methods for highly sensitive AMS measurement of ^{53}Mn, e.g., the gas-filled magnet (GFM) combined with multi-element gas-ionization detector and ΔE-Q3D detection system, have been developed at Munich [1], ANU [2], CIAE-AMS [3] groups, respectively, and the initial exploration for exposure dating has been recently carried out by the Munich and ANU groups, respectively [4,5]. The only significant interfering ions for AMS measurement of ^{53}Mn come from the isobar ^{53}Cr. The electron affinity of manganese is negative so Mn does not form negative ions [6], accordingly molecular ions of MnO^- were conventionally extracted from the cesium sputter ion source in AMS measurement of ^{53}Mn. Since chromium very readily forms negative CrO^- ions and ^{53}Cr has a natural abundance of 9.5%, the interference from ^{53}Cr constitutes a major obstacle for highly sensitive measurement of ^{53}Mn and relevant applications.

In a recent paper, at least three times ^{53}Cr suppression was reported by extracting MnF^-, instead of MnO^-, for AMS measurement of ^{53}Mn [7]. Inspired by this finding, some methods were explored to further determine the suppression of the ^{53}Cr background by the extraction of different manganese molecular ions, and further tap the potential of CIAE-AMS system in the measurement and applications of ^{53}Mn. The experimental setup, performances and results are detailed in this paper.

2. Experimental

2.1. Samples

Commercial MnO_2 and MnF_2 (named C_Blank), commercial $MnO_2 + PbF_2$ (about 1:3 by volume) (named F_Blank) and homemade MnF_2 from commercial MnO_2 (named H_Blank) were used as blank samples, respectively. A laboratory standard with ^{53}Mn/^{55}Mn ratio of 4.47×10^{-11} (CIAE ST) was produced by chemical dilution of a Munich ST, $^{53}\text{Mn}/^{55}\text{Mn} = 2.83 \times 10^{-9}$, provided by Munich group. All samples used were as received without chemical treatment for the removal of chromium. Each sample was mixed with a similar volume of high purity (99.99%) silver powder for improving thermal and electric conductivity and pressed into one of the Al sample holders of a 40-sample NEC MC-SNICS ion source for AMS measurement.

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Table 1
Results of ^{53}Mn/^{55}Mn and ^{53}Cr/^{55}Mn ratios for CIAE ST and a series of blanks, normalized to Munich ST.

Sample code	Sample material	Extraction ion	Normalized ratio (^{53}Mn/^{55}Mn)	Normalized ratio (^{53}Cr/^{55}Mn)	R[a]
Munich ST	$MnO_2 + PbF_2 + Ag$ (1:3:1)	MnO^-	2.83×10^{-9}	9.68×10^{-7}	1.74
		MnF^-	2.83×10^{-9}	5.55×10^{-7}	
CIAE ST	$MnO_2 + PbF_2 + Ag$ (1:3:1)	MnO^-	4.48×10^{-11}	2.46×10^{-7}	2.18
		MnF^-	4.42×10^{-11}	1.13×10^{-8}	
F_Blank	$MnO_2 + PbF_2 + Ag$ (1:3:1)	MnO^-	$<5.88 \times 10^{-13}$	2.13×10^{-7}	2.51
		MnF^-	$\leqslant 6.16 \times 10^{-12}$	8.48×10^{-8}	
C_Blank	$MnO_2 + Ag$ (1:1)	MnO^-	$\leqslant 4.42 \times 10^{-12}$	5.27×10^{-7}	5.98
	$MnF_2 + Ag$ (1:1)	MnF^-	$<2.61 \times 10^{-12}$	8.81×10^{-8}	
H_Blank	$MnF_2 + Ag$ (1:1)	MnF^-	$<2.65 \times 10^{-12}$	5.09×10^{-8}	10.35[b]

Background was estimated from the F_Blank after normalized and corrected for in Munich ST and CIAE ST values.
The efficiency for ^{53}Mn transmission from its negative molecular ions entering the accelerator until ^{53}Mn events being recorded by the ionization chamber is about 0.3% and 0.24% for extraction ions of MnO^- and MnF^-, respectively. These efficiencies consist of two parts: the transmissions of ions with charge state +11 are ~1% and ~0.8% for extraction of MnO^- and MnF^-, respectively, before entering into ΔE-Q3D detection system, and the ΔE-Q3D detection efficiency of about 30% was caused mainly by the Si_3N_4 absorber stripping yield of ions with the charge state +18.

[a] R is suppression ratio of normalized ^{53}Cr/^{55}Mn by extracting MnO^- over that by extracting MnF^-, for each kind of sample material.

[b] Compared with C_Blank of MnO_2.

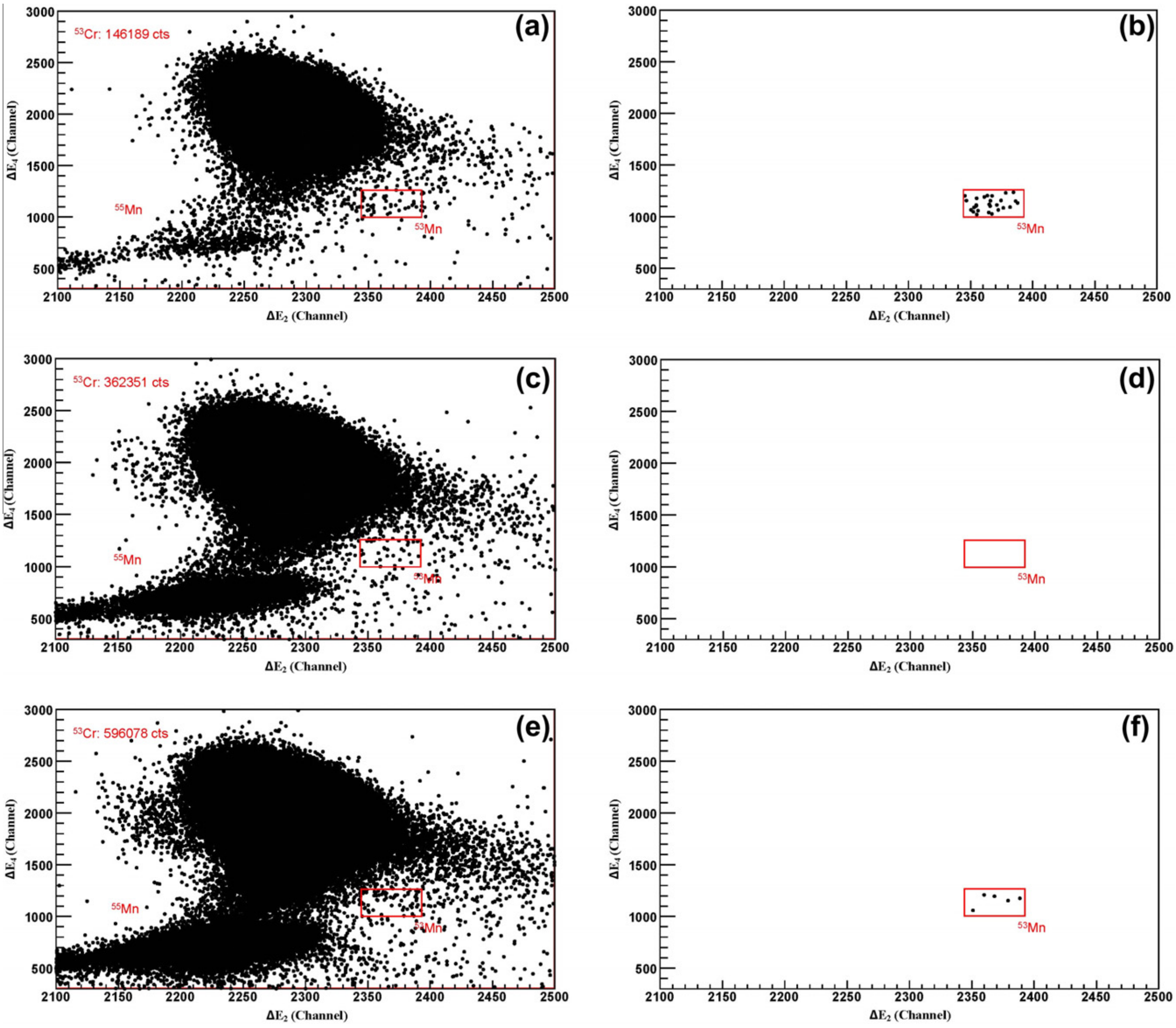

Fig. 1. Two-dimensional spectra of ΔE_2 vs ΔE_4 for one ^{53}Mn standard and two blank samples by MnO^- extraction from ion source (ΔE_2 and ΔE_4 are energy loss signals from anodes 2 and 4, respectively): (a) for a standard sample with ^{53}Mn/^{55}Mn = 4.47×10^{-11}, counting time 1200 s; (c) for a sample of F_Blank ($MnO_2 + PbF_2$), counting time 1800 s; (e) for a sample of C_Blank (MnO_2), counting time 1800s; (b), (d), and (f) are for the same samples as for (a), (c), and (e), respectively, taken with coincidence gated at ^{53}Mn. All samples used were as received without chemical treatment for the removal of Cr.

2.2. Ion injection and acceleration

The negative molecular ions of MnO^- and MnF^- were selected for injection into the HI-13 Tandem Accelerator, and the typical output beam current at the Lower Energy Faraday Cup (LEFC) was about 200 nA for both MnO^- and MnF^-. The negative manganese molecular ions were accelerated by the tandem terminal voltage, which was typically set at 11.5 MV. The foil (3 μg/cm^2 carbon) stripping was employed to break up the molecular ions and produce atomic ions with high charge states. The resulting positively charged ions were further accelerated by the same terminal voltage. A 90° double focusing High Energy Analyzing Magnet (HEAM) with

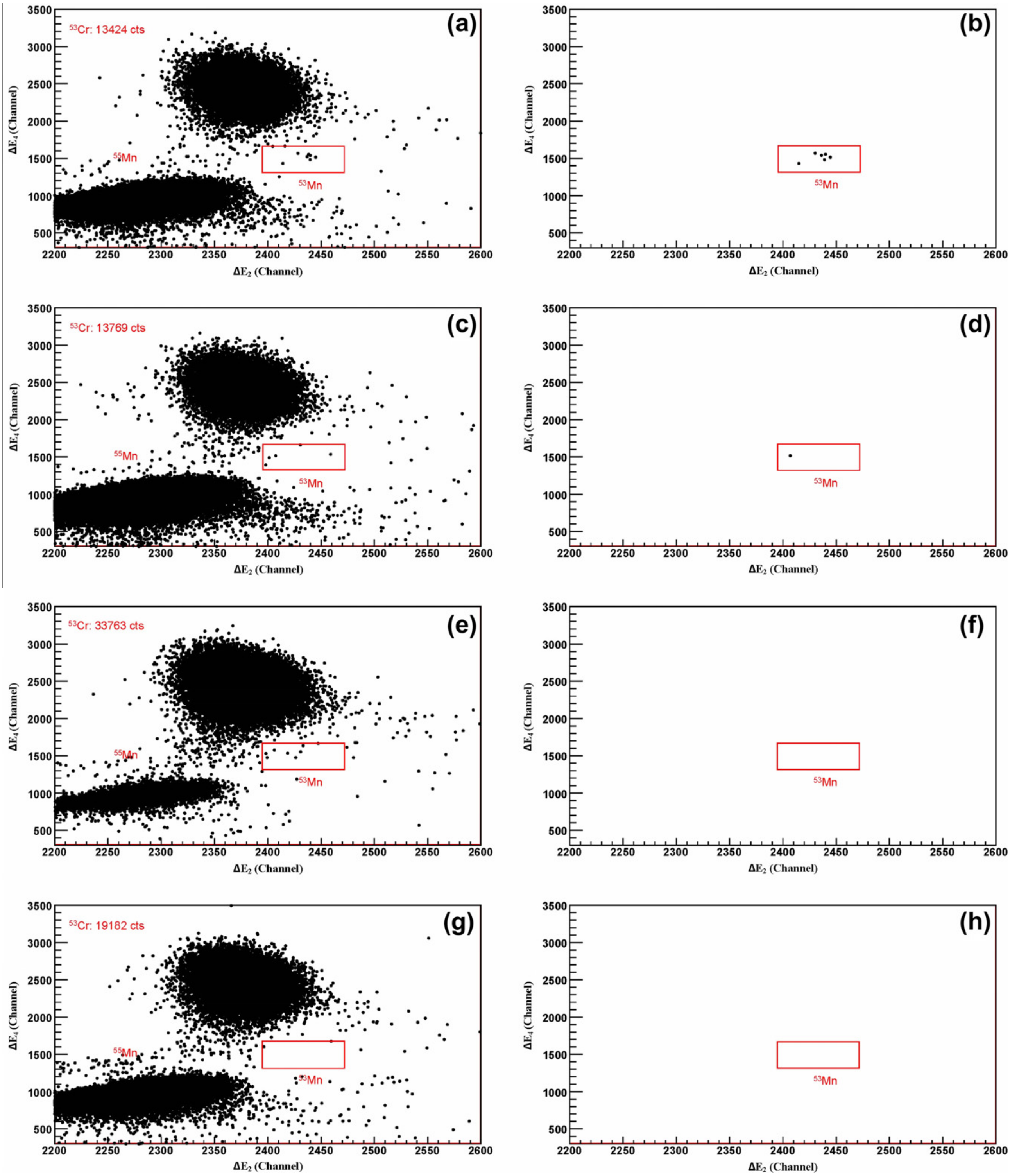

Fig. 2. Two-dimensional spectra of ΔE_2 vs ΔE_4 for one ^{53}Mn standard and three blank samples by MnF^- extraction from ion source (ΔE_2 and ΔE_4 are energy loss signals from anodes 2 and 4, respectively): (a) for a standard sample with $^{53}Mn/^{55}Mn = 4.47 \times 10^{-11}$, counting time 600 s; (c) for a sample of F_Blank (MnO_2 + PbF_2), counting time 600 s; (e) for a sample of C_Blank (MnF_2), counting time 600 s; (g) for a sample of H_Blank (MnF_2, preparation with commercial MnO_2), counting time 600 s (b), (d), (f), and (h) are for the same samples as for (a), (c), (e), and (g), respectively, taken with coincidence gated at ^{53}Mn. All samples used were as received without chemical treatment for the removal of Cr.

a maximal mass energy product of 200 MeV amu was used to select $^{53}Mn^{11+}$ (and $^{53}Cr^{11+}$) with an energy of about 135 MeV. None of these processes can achieve the separation of ^{53}Mn from its stable isobar ^{53}Cr. By means of the switching magnet the particles were transported further to a ΔE-Q3D detection system for the isobar separation of ^{53}Mn and ^{53}Cr and the detection of ^{53}Mn.

2.3. *ΔE-Q3D detection system*

A very homogeneous Silicon Nitride (Si_3N_4) membrane (from Silicon Ltd./UK) with optimal thickness of 4.0 μm (four 1 μm lapped over) was mounted at the entrance of Q3D as an absorber to produce different energy losses for ^{53}Mn and ^{53}Cr. After $^{53}Mn^{11+}$ (and $^{53}Cr^{11+}$) ions passed through the Si_3N_4 membrane, ions with the energy of about 110 MeV and the charge state of 18^+ were analyzed by the Q3D magnetic spectrometer. The isobars of ^{53}Mn and ^{53}Cr were then separated on the focal plane of the Q3D magnet spectrometer according to their different residual energies. The peak distance between ^{53}Mn and ^{53}Cr on the focal plane was about 160 mm. The position separation factors (defined as the ratio of the peak distance to the full-width at half-maximum (FWHM) of each peak) for peak position was 2.6 for the Si_3N_4 foils with thicknesses of 4 μm. In order to increase the detection efficiency for measuring medium mass nuclides and further separation of isobaric interferences, a multiple-anode ionization chamber (MAIC, four anodes in this work) with an entrance window of 100 × 40 mm^2 Mylar foil was mounted at the accurately located position of the Q3D focal plane to record the events of the nuclide of interest. The ionization chamber was filled with 38–40 mbar propane for the measurement of ^{53}Mn. By suitable choice of the magnetic field, a suppression factor of about 10^4 can be achieved for ^{53}Cr ions, while most of the ^{53}Mn ions are recorded by the MAIC [8].

3. Results and discussion

The Munich ST and CIAE ST were first measured for the optimization of measurement conditions, for their relatively high ratios of $^{53}Mn/^{55}Mn$. The results of $^{53}Mn/^{55}Mn$ ratios for all samples were obtained by simultaneously measuring the currents of $^{55}MnF^-$ (or $^{55}MnO^-$, when MnO_2 sample was used) ions on the low energy Offset Faraday Cup, and the count rate of ^{53}Mn recorded by the MAIC (after treated by software gated coincidence and background subtraction). The results of $^{53}Cr/^{55}Mn$ ratios were obtained in the same way as for $^{53}Mn/^{55}Mn$, except that the count rate of ^{53}Cr was directly recorded by the MAIC without software gate coincidence. The ratios of $^{53}Mn/^{55}Mn$ and $^{53}Cr/^{55}Mn$ were both normalized by the Munich ST. Preliminary results for these samples are presented in Table 1.

3.1. *Comparison between MnO^- and MnF^- injection*

In the ΔE-Q3D system the combination of the Q3D magnet and the MAIC brought about a very efficient suppression of interfering ^{53}Cr ions. Theoretically, the suppression factor of ^{53}Cr should be the same for extracting MnO^- and MnF^- in ΔE-Q3D detection system due to their almost equal injection energy and energy loss after passing through the absorber. As shown in Table 1, however, the ratio of $^{53}Cr/^{55}Mn$ by extracting MnF^- is several times lower than that by extracting MnO^-. It implies that ^{53}Cr may be suppressed by a factor of about 2–10 by extracting MnF^- in place of MnO^- in ion source. This result is consistent with Ref. [7].

3.2. *Sensitivity of ^{53}Mn measurements*

The suppression of ^{53}Cr in the ionization chamber critically depends on the proper settings of software windows, which can be optimized by using a sample with relatively high ^{53}Mn content, Munich ST sample. These settings were then applied for the measurements of ^{53}Mn in CIAE ST and a series of blank samples. The results of energy loss signal from anode 2, ΔE_2, versus that from anode 4, ΔE_4, are shown in Figs. 1 and 2. As shown in (b, d, f) of Fig. 1 and (b, d, f, h) of Fig. 2, nearly all ^{53}Cr counts can be rejected with the software windows for blank samples. For the CIAE ST sample, the ^{53}Mn counts can be reliably extracted by two-dimensional coincidence gated on proper anodes of the MAIC. On the other hand, figures for all blank samples show there are only 0–5 events in $M = 53$ window after software gate coincidence, corresponding to a ^{53}Cr suppression factor of about 10^5 in the ionization chamber, based on the total ^{53}Cr counts of 10^5.

In general, a total suppression factor of about 10^9 can be obtained by a combination of the Q3D magnet and the ionization chamber. In other words, a detection limit of 10^{-15} or even lower is reachable for AMS measurement of ^{53}Mn with the ΔE-Q3D detection system, if the content of chromium in a sample could be reduced to less than 10^{-6} (ppm) level by chemical treatment and the extraction of MnF^- ions from ion source is adopted.

4. Summary

Methods for highly sensitive AMS measurement of ^{53}Mn were explored by extracting different Mn-containing molecular ions in ion source and using different chemical forms of sample materials. Preliminary results indicate that: (1) The ^{53}Cr suppression factor for MnF_2 sample and MnF^- ion extraction is 5–10 times larger than that for MnO_2 sample material and MnO^- ion extraction; (2) When the sample material of $MnO_2 + PbF_2$ is used, ^{53}Cr suppression factor by extracting MnF^- is two times higher than that by extracting MnO^-. The use of $MnO_2 + PbF_2$ as sample material not only simplified sample preparation (laboratory synthesis of MnF_2 is not needed), but also improved the sensitivity for AMS measurement of ^{53}Mn. The extraction of MnH^- ions from ion source is going to be tested for AMS measurement of ^{53}Mn, and that may bring about a further ^{53}Cr suppression of more than two orders of magnitude, estimated on the basis of the data from the Negative-Ion Cookbook [6].

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