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Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Nuclear-chemical synthesis of iron compounds and their Mössbauer identification

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Abstract

The investigation of iron chemistry is of great technological as well as intellectual importance to humanity. Iron is known to exhibit a wide range of oxidation states, but some potentially accessible oxidation states and simple binary compounds remain unknown. Their synthesis is a challenge of both theoretical and practical importance. Nuclear-chemical synthesis constitutes an interesting alternative to conventional synthesis, by radioactive decay of another nucleus in a stable chemical compound to yield the desired element in conserved, and hence potentially unfamiliar, chemical surroundings and oxidation states. This approach allows targeting those iron derivatives, which are difficult to synthesize by common chemical routes due to both kinetic and thermodynamic reasons. In this context, ⁵⁷Mn is a very interesting nuclide because manganese shows a very wide range of



oxidation states, which could furnish unknown oxidation states and binary compounds of iron. The main goal of the suggested project is a nuclear-chemical synthesis and Mössbauer identification of different iron compounds originating from parent compounds of manganese using the nuclear transformation $^{57}\text{Mn} (T_{1/2} = 85.4 \text{ s}) \rightarrow ^{57}\text{Fe}$. The primary objective is to observe as yet unknown and/or less-common oxidation states of iron as well as novel iron containing compounds. The recorded Mössbauer parameters, will be compared to parameters of iron compounds in the literature, as well as computationally derived ones.

Requested shifts: 14 shifts, (split into 3 runs over 3 years)

Introduction

Iron is one of the most abundant elements in nature (both in the Earth crust and in the Solar system). The total number of the known minerals now exceeds 5000, 1/5 of them being iron minerals [1].

Iron is an indispensable element of biological processes. “It is safe to say that, with only a few possible exceptions in bacterial world, there would be no life without iron.” [2]

Iron also is of tremendous value for the present-day engineering. It is not possible to imagine the modern electronics/spintronics without iron compounds. It is the main component of steels and cast-irons, which are today the main structural materials and constitutes the active catalyst in large scale processes such as the Haber-Bosch process. Thus, the research of iron chemistry is of critical importance for the humanity progress.

In Earth’s crust, iron is present mainly as compounds, in oxidation states +2 and +3. However, several other oxidation states have been synthesized. It is important that the compounds containing iron in unusual oxidation states can show unique properties even when iron content is small. The most spectacular example is amethyst, which purple colour is determined by ~100 ppm of iron(IV) impurities [3]. It was also found that iron in rare oxidation states can be observed in the industrial processes as intermediates and by-products [4,5].

Also, the application of iron compounds in high (>3+) oxidation states is now seriously considered for some industrial use for the electric batteries [6,7] and in the water treatment technology [8,9]. Thus, the investigation of iron in different oxidation states, including uncommon ones, is of considerable practical importance.

The synthesis and the study of iron in different oxidation states are certainly of greatest interest and importance for the fundamental chemistry. It is known that all 3d-elements from scandium to manganese show a range of positive oxidation states (zero oxidation state and some negative states are also known but less common for metals). Iron and the following 3d-elements have more electrons in their valence shells, but show less diversity of oxidation states. While oxidation states +7 and +8 are well-known for ruthenium and osmium, which are of the heavy 4d, and 5d congeners of iron in the Periodic System, and data on oxidation state +9 for iridium (congener of cobalt) are published [10], there are no reliable data supporting the existence of iron in oxidation states higher than +6. Thus, observation of the Fe(VII)O_4^- ion would break the known range of oxidation-states for iron and would by itself constitute a very impactful result. It is, however, clear that the synthesis of these high oxidation states is a difficult experimental problem. Therefore, it is necessary to look for the alternative ways for the synthesis of such compounds.

One of the possible ways is the nuclear-chemical synthesis. It consists of the synthesis of iron from another element present in stable compound while preserving the chemical arrangement and oxidation state. This approach can allow one to obtain those less stable iron compounds, which are difficult to synthesize by common chemical ways due to kinetic and other reasons.

The main goal of the suggested project is to document different oxidation states of iron using nuclear-chemical synthesis of different iron compounds from the compounds of manganese using the nuclear transformation $^{57}\text{Mn} (T_{1/2} = 85.4 \text{ sec.}) \rightarrow ^{57}\text{Fe}$ and their identification by emission Mössbauer spectroscopy. Initial experiments will target Fe(V)O_4^{3-} , Fe(VI)O_4^{2-} , and Fe(VII)O_4^- by decay from their manganese analogues. The simplicity of these systems and the fact that tetraoxoferrate(VI) is very thoroughly characterized by a range of techniques including Mössbauer spectroscopy, make them perfectly suited as test systems. Furthermore, much of the interest in high-valent iron chemistry concerns iron-oxo complexes, so-called ferryl groups, and their electronic structure and reactivity, in which context these systems are directly relevant. Calculation of the spectroscopic properties using theoretical electronic structure methods will be used to substantiate the interpretation of the experimental data.

Mössbauer spectroscopy

Mössbauer spectroscopy is an important and singular analytical tool in chemistry, which can be used to determine probe atoms charge (oxidation) state, site symmetry and magnetic interactions through the hyperfine interaction and information on binding properties can be determined from the Debye-Waller factor.

The possibility to study iron by Mössbauer spectroscopy is extremely important and, in fact, unique. Mössbauer spectroscopy can be applied for many elements. However, it provides for iron (for its isotope ^{57}Fe) amongst the highest level of information: the effect is well-observed at room temperature, the measurements need rather simple experimental arrangement, different oxidation states are well-recognized, the spectra are simple to deconvolute and interpret. It is well known that this technique allows one to observe phenomena impossible to be observed by other methods.

^{57}Mn emission Mössbauer spectroscopy has been known since 1975, when Preston and Zabransky published the first paper [11]. They applied the nuclear reaction $^{54}\text{Cr}(\alpha, p)^{57}\text{Mn}$ to synthesize the source of ^{57}Mn in Cr_2O_3 matrix. In 1992 Nakada et al. [12] used the same reaction to get the sources from metallic chromium, Cr_2O_3 and CrO_3 . Later, the alternative approach to produce the ^{57}Mn sources by ion-implantation of ^{57}Mn into substance was developed in ISOLDE [13] and RIKEN [14]. The peculiarity of both approaches is the complicated chemistry, which accompanies the stabilization of ^{57}Mn ions after ^{54}Cr decay or the stabilization of ^{57}Mn ions in the implantation process as well as the radiolysis of the substance. The half-life time of ^{57}Mn is quite short (85.4 s). Therefore, it is challenging to conduct the common chemical synthesis with it. However, such a synthesis could be realized using convincing chemical reactions.

Chemical reactions with ^{57}Mn

The simplest way to involve implanted manganese into chemical reaction is to heat-up the target. This approach was already applied for several matrices (see Table 1). But the matrices used were quite chemically inert. Therefore, implanted manganese ions transform into most typical and stable form adapting in the matrix structure (with possible local change of this structure). This can also explain the fact that the spectra obtained were commonly quite complicated due to the presence of several forms of ^{57}Fe , magnetic effects being also observed.

When ^{57}Mn is implanted into compounds of transition elements in oxidation states greater than +3 (e.g. TiO_2 [15], CrO_3 [12], KMnO_4 [16]), no isovalent substitution of the transition element by manganese was reliably observed (see Table 1) either the natural charge state of iron is associated with an electron hole (TiO_2) or implantation damage/defects control the valence state.

In the proposed project, we suggest to involve ^{57}Mn into the reaction with an active chemical compound to synthesize the compound of definite composition and structure with manganese in a wide range of oxidation states. In particular, we plan to synthesize $^{57}\text{Mn}^{+7}$, in the form of MnO_4^- , which may be transformed into Fe^{+7} during the decay. Note, that oxidation state +7 of iron is now unknown! Such researches with ^{57}Mn have never been conducted before. For reference we will also target synthesis of MnO_4^{2-} , which should yield the stable form of hexavalent iron (FeO_4^{2-}) that has been extensively studied by conventional Mössbauer spectroscopy.

Table 1

Results of $^{57}\text{Mn}^+$ implantation in some oxide matrices containing host metal in different oxidation states [12,15,16-24]

Host metal oxidation state	Matrix	Result
2+	ZnO [17], MgO [18,19]	Fe^{2+} found, Fe^{3+} observed as due to acceptor defects.
3+	$\alpha\text{-Al}_2\text{O}_3$ [20,21], In_2O_3 [22], $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ [23]	Stability of Fe^{3+} verified, Fe^{2+} found as consequence of the implantation process.
4+	TiO_2 [15], SnO_2 [24]	Max. 3+ observed as the natural Fe charge state (associated with electron holes).
5+	no example	
6+	CrO_3 [12]	Fe^{3+} found.
7+	KMnO_4 [16]	Mainly Fe^{2+} . Fe^{8+} was also declared.

General Methodology

^{57}Mn is a radioactive nuclide with half-life time of 85.4 s. This establishes the time limitation for chemical treatment and consequently determines the experimental methodology. To achieve the goals indicated above, it is required to realize three experimental steps: Collecting the necessary ^{57}Mn activity at the ISOLDE beam line, conducting the chemical sample preparation, and recording the Mössbauer spectrum.

The current ISOLDE ^{57}Mn beam fluence rate is $2 \cdot 10^8$ nuclei $\cdot\text{s}^{-1}$. This determines the maximal target activity: 0.2 GBq (5.4 mCi), which decreases during chemical synthesis and spectrum recording. This may require repeated measurements to obtain the Mössbauer spectrum of acceptable quality. Thus, we need a procedure to realize the three mentioned experimental steps repeatedly and sequentially. For the optimal use of the beam facilities one should find optimal conditions for each step and make them compatible. The result should allow us to record emission spectra with maximal efficiency fulfilling both radiation safety and chemical safety requirements. This will be achieved as described in the following section.

In the current experimental setup available for emission Mössbauer spectroscopy at ISOLDE/CERN [25], we have target exchange equipment that can be used to remove targets (samples) from the vacuum through a small sample exchanger. A sample can be removed from the setup ~ 5 -10 seconds after the halt of implantation, and a new implantation can start ~ 30 seconds after the halt of the previous implantation.

We suggest two approaches for a sample preparation. The first approach means transformation of ^{57}Mn into water solution and Mössbauer measurement of a frozen sample. The second approach is to introduce ^{57}Mn into solid-state reaction.

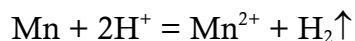
Wet chemistry with ^{57}Mn

^{57}Mn accumulation for wet chemistry

In order to make wet chemistry with ^{57}Mn , one needs to get solution containing $^{57}\text{Mn}^{2+}$ ions. Several options for transfer have been tested, and the most promising one is to implant ^{57}Mn into a thin layer ($\sim 0.1 \mu\text{m}$) of metal (Mn, Mg, Zn, etc.) deposited on a chemically inert plate (Cu, glass, noble metals, etc.). After implantation, the layer is washed away by acid getting solution of $^{57}\text{Mn}^{2+}$ ready for the chemical reaction. Different options are being explored, but in tests $0.1 \mu\text{m}$ Mn layer on Cu-foil was removed immediately and completely in 1M H_2SO_4 . This acid concentration is convenient for the chemical experiments proposed.

Chemistry with ^{57}Mn solutions

The above-mentioned dissolution of metallic manganese layer containing implanted ^{57}Mn by acid is the first chemical reaction which should be studied:



It is necessary to document the ^{57}Fe Mössbauer parameters obtained of samples of aqueous $^{57}\text{Mn}^{2+}$, because it may be present in the sample after the chemical reactions. The second suggested reaction is the oxidation of Mn^{2+} to permanganate-ion (MnO_4^-) which contains Mn^{7+} . This key experiment should clarify the possibility to obtain heptavalent iron by nuclear-chemical reaction. 1M H_2SO_4 is exactly the medium recommended to oxidize manganese to permanganate. This reaction has widely been used for many years in analytical chemistry for the determination of manganese e.g. by photometry. Therefore, the optimal chemical conditions for this reaction are well known. It is favourable that permanganate-ion have very intense violet colour, which is seen when we have ^{57}Mn with enough carrier. Therefore, it is simple to visually confirm that the reaction takes place.

The best oxidizer seems sodium bismuthate(V) (NaBiO_3):



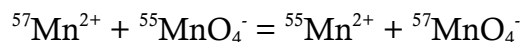
This reaction takes place quite quickly both at room and at higher temperature despite the reactions with other oxidizers. The disadvantage could be incomplete oxidation. But Mössbauer lines of Fe^{2+} (coming from Mn^{2+}) and the line(s) of Fe^{+7} (e.g. FeO_4^- coming from MnO_4^-) are expected at distinctly different energies (Doppler velocity in Mössbauer spectroscopy) in the Mössbauer spectra and therefore easily distinguishable. Therefore, the detection of even a small constituent of Fe^{+7} is considered to be a success.

The concentration of the carrier (^{55}Mn) can be easily varied. This allows us to watch the influence of manganese concentration on the reaction products. Such observation can be interesting for analytical chemistry.

A similar approach will be used to study other reactions with a purpose to obtain different species of manganese in different oxidation states, see Table 2 for the planned reactions.

Isotopic exchange

A specific type of the reactions which can be tested within this project is isotopic exchange. It is known, that the exchange reaction speed depends on chemical state of the exchanging ions. We can try to observe the exchange mixing obtained $^{57}\text{Mn}^{2+}$ solutions with another manganese species. As an example, it is interesting to study the exchange reaction



probing the influence of $^{57}\text{Mn}/^{55}\text{Mn}$ ratio on the exchange yield.

This type of the reactions is considered as a new possible way for the analysis of manganese-containing substances. In case of successful observation of the exchange phenomenon in simple systems we shall expand this approach to more sophisticated substances including those organo-manganese compounds where fast manganese exchange is possible.

Precipitation of MnO₂

Precipitation of MnO₂ in neutral solutions is well-known reaction of manganese. This reaction can allow us to obtain daughter iron in tetravalent state. Note, iron dioxide (FeO₂) is not known! The primary identification of solid Mn(Fe)O₂ can be done by room temperature Mössbauer spectroscopy followed by common techniques (after full ⁵⁷Mn decay). The result obtained will be compared with the result of direct implantation of ⁵⁷Mn⁺ into MnO₂, which will also close the gap in the series of known dioxides of the first row transition elements. Subsequently, other dioxide substrates for the implantation can be envisaged and this approach will then constitute a new venue for the study of these materials, some of which, *e.g.* TiO₂ and CoO₂, are of great importance in photochemical and electrochemical energy processes [26,27]. Eventually, implantation in dioxides will also make possible the study of magnetic phases (CrO₂) [28] and systems with exotic electronic structures originating from large spin-orbit coupling (IrO₂) [29].

Table 2

Reactions for studying the formation of different oxidation states of manganese in solutions

	Carrier, pH etc.	Reaction
1a	no carrier (-)	$\text{Mn} + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2\uparrow$ (with 1M H ₂ SO ₄)
1b	MnSO ₄ , 10 ⁻⁵ M	
1c	MnSO ₄ , 0.01M	
2	-	$\text{Mn} + \text{HNO}_3 \rightarrow \text{Mn}^{2+} + \dots$ (with 1M HNO ₃)
3a	-	$2\text{Mn}^{2+} + 5\text{NaBiO}_3 + 14\text{H}^+ = 2\text{MnO}_4^- + 5\text{Na}^+ + 5\text{Bi}^{3+} + 7\text{H}_2\text{O}$
3b	MnSO ₄ , 10 ⁻⁵ M	
3c	MnSO ₄ , 0.01M	
4a	MnSO ₄ , 0.01M	$\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{OH}^- \rightarrow \text{MnO}_4^{2-} + \text{CO}_3^{2-} + \text{H}_2\text{O}$ (with NaOH) $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{MnO}_2\downarrow + \text{CO}_2\uparrow$ (in neutral solution)
4b	MnSO ₄ , 2M	
5a	-	$\text{MnO}_4^- + \text{SO}_3^{2-} + \text{OH}^- \rightarrow \text{MnO}_4^{2-} + \text{SO}_4^{2-} + \text{H}_2\text{O}$ (with NaOH)
5b	MnSO ₄ , 10 ⁻⁵ M	
5c	MnSO ₄ , 0.01M	
6a	-	$\text{MnO}_4^- + \text{SO}_3^{2-} + \text{OH}^- \rightarrow \text{MnO}_4^{3-} + \text{O}_2 + \text{H}_2\text{O}$ (with strong NaOH)
6b	MnSO ₄ , 0.01M	
7a	-, pH=7	$\text{Mn}^{2+} + \text{H}_2\text{O}_2$ (30-50%) + NaOH → Mn ³⁺ / Mn ⁴⁺ (<i>e.g.</i> MnO ₂)
7b	-, pH=9	

7c	-, pH=14	
7d	MnSO ₄ , 0.01M, pH=7	
7e	MnSO ₄ , 0.01M, pH=9	
7f	MnSO ₄ , 0.01M, pH=14	
8	MnSO ₄ , 0.01M, pH=0 MnSO ₄ , 0.01M, pH=1 MnSO ₄ , 0.01M, pH=3 MnSO ₄ , 0.01M, pH=7 MnSO ₄ , 0.01M, pH=9	$^{57}\text{Mn}^{2+} + ^{55}\text{MnO}_4^- = ^{55}\text{Mn}^{2+} + ^{57}\text{MnO}_4^-$ (isotopic exchange in different media) in acidic should be observed.

⁵⁷Mn emission Mössbauer spectroscopy of ⁵⁷Mn frozen solutions

The measurement of frozen solutions (0°C - -196 °C) is not a new approach for Mössbauer spectroscopy [30]. The Mössbauer parameters of frozen solutions correlate well with the parameters of solid samples. Therefore, the isomer shifts obtained can be easily compared with known values and reflects both oxidation state of iron and its coordination environment.

To keep an absorption of 14.4 keV Mössbauer photons in ice at <15% level, 2-3 mm ice layer is appropriate. Basically, the cooling plate has a diameter of 1 cm, this would mean ~0.2 cm³. If this volume will be insufficient to conduct the chemical reactions reproducibly which will be observed in Mössbauer spectra, the sample volume will be increased, which could lead to additional time for the experiments.

Additional research of the solutions

To specify the average initial content of manganese in the studied solutions, to analyse the impurities etc. the samples after Mössbauer measurements could be collected. After full decay the collected solutions can be studied by common chemical techniques.

Solid-state reactions with ⁵⁷Mn

We believe that the use of chemically active matrices is a simple route to the synthesis of ⁵⁷Mn-doped compounds containing manganese in a wide range of oxidation states. We plan to test several reactions which we already successfully used to synthesize the compounds of ⁵⁷Fe and ⁵⁷Co [31-33] (see Table 3).

Table 3

Tentative products of the solid-state reactions of alkali metal oxides with ⁵⁷Mn and oxides of some other transition metals

	Li ₂ O ₂	Na ₂ O ₂	KO ₂	RbO ₂	CsO ₂
Mn-57 without carrier	Mn ³⁺	Mn ⁴⁺	Mn ⁵⁺	Mn ⁵⁺	Mn ⁵⁺

and any additional reactant					
Mn-57 with carrier Mn	LiMnO ₂	Na ₄ MnO ₄	K ₃ MnO ₄	Rb ₃ MnO ₄	Cs ₃ MnO ₄
Mn-57 with carrier Mn ₂ O ₃	LiMnO ₂	Na ₄ MnO ₄	K ₃ MnO ₄	Rb ₃ MnO ₄	Cs ₃ MnO ₄
Mn-57 with carrier MnO ₂	LiMnO ₂	Na ₄ MnO ₄	K ₃ MnO ₄	Rb ₃ MnO ₄	Cs ₃ MnO ₄
Mn-57 without carrier + Fe	LiFe(Mn)O ₂	Na ₄ Fe(Mn)O ₄	K ₃ Fe(Mn)O ₄	Rb ₃ Fe(Mn)O ₄	Cs ₃ Fe(Mn)O ₄
Mn-57 without carrier + Fe ₂ O ₃	LiFe(Mn)O ₂	Na ₄ Fe(Mn)O ₄	K ₃ Fe(Mn)O ₄	Rb ₃ Fe(Mn)O ₄	Cs ₃ Fe(Mn)O ₄
Mn-57 without carrier + CoO	LiCo(Mn)O ₂	Na ₄ Co(Mn)O ₄	K ₃ Co(Mn)O ₄	Rb ₃ Co(Mn)O ₄	Cs ₃ Co(Mn)O ₄
Mn-57 without carrier + Cr ₂ O ₃	LiCr(Mn)O ₂	Na ₄ Cr(Mn)O ₄	K ₂ Cr(Mn)O ₄	Rb ₂ Cr(Mn)O ₄	Cs ₂ Cr(Mn)O ₄

The first type of the reactions, which could be tested is the oxidation of ⁵⁷Mn in the matrix of alkali metals peroxides or superoxides (MO_x). These oxides contain active oxygen which allows one to oxidize manganese at moderate heating. According to the manganese chemistry such interactions lead to manganese(IV), (V) and (VI). To make such tests ⁵⁷Mn can be implanted into the solid melt of MO_x. Then, the short-time heating should be quickly done to transform manganese into MnO₄ⁿ⁻-ions, n=2,3,4. Despite high chemical activity of the peroxides and superoxides, many of them are melted at high temperatures and are stable while melting. The oxidation of the transition metal takes place locally. Thus, the reactions can be cyclically repeated with the same target.

The second type is the reactions with the mixture of alkali metal peroxides or superoxides and transition metals (metal powder, oxides, etc.). In this case, the chemical behaviour of implanted ⁵⁷Mn is determined by the matrix of the synthesizing metallates (chromates, manganates, ferrates, cobaltates, etc.). But to repeat the synthesis a fresh mixture should be used.

Quantum chemical calculations of Mössbauer parameters

The calculation of both the isomer shift and the quadrupole splitting is nowadays possible at the level of density functional theory with modern quantum chemical programs such as ORCA [34] and Dalton [35] or DIRAC [36] if the treatment of relativistic effects is necessary. For smaller compounds it is even possible to calculate them at the state-of-the-art level of Coupled Cluster Theory [37]. We plan therefore to support the interpretation of the

measured Mössbauer spectra by such quantum chemical calculations and in particular to study the dependence of the Mössbauer parameters on the oxidation states.

Feasibility

ISOLDE has in recent years, always been able to deliver $>2 \cdot 10^8$ $^{57}\text{Mn}/\text{s}$ beams needed. The Mössbauer collaboration has access to all implantation facilities and on/off line Mössbauer setups needed. These experiments will be rather labor demanding, it is estimated that 4-5 persons are required to run the measurements. In recent years, >10 persons have attended ^{57}Mn eMS beam-times, so this is not expected to be a problem.

Main suggested chemical reactions were already tested in the environment like that at ISOLDE with the same timing.

At ISOLDE, we have access to most of the standard chemicals needed including all mentioned in this proposal. We have already prepared in sufficient quantity and tested the Mn/Cu foil necessary for wet-chemical approach. Other chemicals, glassware etc. will be brought in as needed.

Conclusions

During and after completing the experimental proposal outlined here, the prospects of performing chemical syntheses with short lived isotopes will have been demonstrated. This will open up new ideas of extending this work, in for example biochemistry. In biology, Mn^{2+} function as cofactors for a large variety of enzymes and are essential in detoxification of superoxide free radicals in organisms. This project may provide a new analytical method within this field of study.

Summary of requested shifts:

With calibration ($\sim 20\%$ from experience) and contingency ($\sim 20\%$) we amount to 14 shifts required. We estimate that 2-3 years will be required. The first year, we will collect as much data as possible with the chemical that are ready, and based on the results, optimize the experimental plan for the following years.

We plan that the first run will be started with the wet-chemical reaction according to Table 2. The shapes of the respective Mössbauer spectra are difficult to predict. To detect all possible peculiarities, it is required to measure the spectra in two velocity ranges. If the

spectra are complicated by the relaxation phenomena (which is observed quite frequently in frozen solutions [18]), the measurements at different temperatures and in applied magnetic field are strictly desirable. Such measurements are planned to be performed mainly during the second run after necessary preparations. The second run will be also devoted to measurements of solid-state syntheses products.

We request 5 shifts for the second run to complete the measurements of Table 2 with any necessary corrections and Table 3. If time will be insufficient, some reactions of Table 3 will be skipped.

The third run is planned (4 shifts requested) to devote mainly to the measurements of samples coming from different chemical, biological and other fields, which will be selected during the first two years according to the accumulated experience. In case of necessity, some additional measurements to verify the previous results can be also done.

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
[if relevant, name fixed ISOLDE installation: COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH]	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification
On-line eMS chamber	<input checked="" type="checkbox"/> Existing <input type="checkbox"/> New	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified <input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
[Part 2 experiment/ equipment]	<input type="checkbox"/> Existing <input type="checkbox"/> New	<input type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified <input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards			
	[Part 1 of the experiment/equipment]	[Part 2 of the experiment/equipment]	[Part 3 of the experiment/equipment]
Thermodynamic and fluidic			
Pressure	Ambient		
Vacuum	Yes		
Temperature	110 K - Room temperature		
Heat transfer	N/A		
Thermal properties of materials	N/A		
Cryogenic fluid	LN, 1 Bar, 2-3 l		
Electrical and electromagnetic			
Electricity	~600 V, current negligible (detectors)		
Static electricity	N/A		
Magnetic field	N/A		
Batteries	<input checked="" type="checkbox"/>		
Capacitors	<input type="checkbox"/>		

Ionizing radiation			
Target material	Metals		
Beam particle type (e, p, ions, etc)	Ions		
Beam intensity	$\sim 2 \times 10^8 \text{ s}^{-1}$ (^{57}Mn)		
Beam energy	30 keV		
Cooling liquids	LN		
Gases	N/A		
Calibration sources:	<input type="checkbox"/>		
• Open source	<input type="checkbox"/>		
• Sealed source	<input checked="" type="checkbox"/> 9001:2015		
• Isotope	^{57}Co		
• Activity	$\sim 10 \text{ MBq}$		
Use of activated material:			
• Description	<input type="checkbox"/>		
• Dose rate on contact and in 10 cm distance	10 cm: 244 $\mu\text{Sv/h}$ 30 cm: 27 $\mu\text{Sv/h}$		
• Isotope	^{57}Mn		
• Activity	$\leq 0.2 \text{ GBq}$		
Non-ionizing radiation			
Laser	None		
UV light	None		
Microwaves (300MHz-30 GHz)	None		
Radiofrequency (1-300MHz)	None		
Chemical			
Toxic	[chemical agent], [quantity]		
Harmful	H2SO4, 1l		
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	H2SO4, 1l		
Irritant	[NaBiO3, 100g]		
Flammable	[chemical agent], [quantity]		
Oxidizing	NaBiO3, 100g		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	Chemical waste, see below		
Mechanical			
Physical impact or mechanical energy (moving parts)	N/A		
Mechanical properties (Sharp, rough, slippery)	None		
Vibration	None		
Vehicles and Means of Transport	N/A		
Noise			
Frequency	N/A		
Intensity	N/A		
Physical			
Confined spaces	GPS/GLM area		
High workplaces	None		
Access to high workplaces	N/A		
Obstructions in passageways	None		
Manual handling	GPS/GLM area		

Poor ergonomics	N/A		
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3.1 Hazard identification

3.1.1 Radiation

The risk for the personal removing implanted targets will be minimized by use of appropriate personal protective equipment. This includes (disposable) lab coats, gloves, visors covering face, safety shoes, and helmets. Radiation doses will be monitored using personal and active dosimeters. Any possibility of contamination after each risk operation will be monitored by use of the hand-foot monitors before leaving the hall.

However, the personal will be exposed to ionizing radiation when transferring samples from the on-line setup and preparing samples to be measured off-line. This is from max. 0.2 GBq (5.4 mCi) source containing ^{57}Mn ($T_{1/2} = 1.5$ min.). The relevant radiation is 2.5 MeV β (endpoint) and γ 's. The worst γ is 5.5%/Bq 692 keV, which gives 11 $\mu\text{Sv/h}$ dose rate at 30 cm distance (closest working position). The total dose rate from gammas is 27 $\mu\text{Sv/h}$ at 30 cm distance. The dose rate from β is negligible, as target surfaces are orientated away from the personal during dismounting.

During removal of implanted target, the person can be exposed for duration of max. 5 seconds at a distance >30 cm. Thereafter samples are dropped into chemical flasks that are lead shielded.

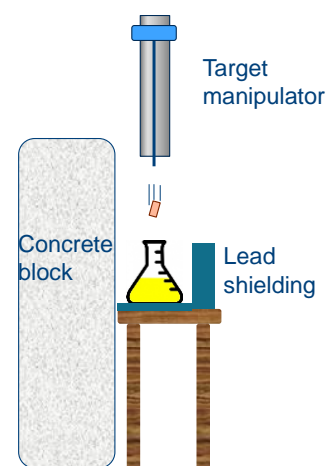


Figure 1: Illustration of handling of radioactive samples. The person handling the sample is behind the Lead shielding, non-essential personal are behind the concrete block.

After the chemistry, radioactive liquid samples are removed with pipette and put on a cold finger where they are immediately frozen before being put in front of the spectrometer. Although most of this is done behind appropriate shielding (~ 5 cm lead), a ≤ 5 sec. exposure at ≥ 30 cm cannot be avoided.

In total, a person is manipulating samples in close proximity (≥ 30 cm) ≤ 10 seconds every 10 minutes. This would result in accumulated dose of ≤ 4 μSv during a 8 hour shift, and total of ~ 50 μSv during a ~ 5 day experiment. This dose would, however, be shared between several persons.

If due to mistake, a radioactive source is dropped on the floor, and not found immediately, persons will be guided out of the area for ~ 20 minutes while it decays sufficiently to be of no hazard. All chemical spills will be neutralized immediately by respective agents. Exact protocols for performing the measurements will be written, and all personal involved trained in the handling.

The purity of the ^{57}Mn beam provided at ISOLDE has been measured MR-TOF [Wolf12] of the ISOLTRAP experiment [Kreim13], where only stable ^{57}Fe impurities less than 1/5000 were detected. γ -ray spectroscopy performed on ^{57}Mn implanted samples the day after implantation has

not revealed measurable activity from long lived isotopes. This means that after sufficient decay, liquids can be disposed of as non-radioactive waste.

Chemical waste will be packed properly in plastic containers/tubes after the beam time. A list of items with quantity will be provided and fixed to the plastic box that will be used for packaging. The UN number and the list should be fixed on the box. The transport to the CERN chemical products store (Building 262) will be requested through the edh system. The RP team will check individual items before the transport.

3. 1.2. Chemical safety

All chemicals will be in appropriate flask and/or beakers behind appropriate lead shielding. Transfer of liquid chemicals takes place. All handling will be done using appropriate safety clothing. All chemical reactions will be tested off-line before being employed at ISOLDE. Some reactions are exothermic, but the heat evaluation is negligible due to low concentrations of reacting substances.

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): (make a rough estimate of the total power consumption of the additional equipment used in the experiment)

Standard electronics and computers all using 220 V and max 1 A.

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