

Three solid circles are arranged horizontally: a blue circle on the left, an orange circle in the middle, and a blue circle on the right.

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Increasing the negative ionization yield for the
efficient detection of ^{233}U and ^{236}U by AMS

February 2022

DOI: [10.5281/zenodo.6256795](https://doi.org/10.5281/zenodo.6256795)

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ABSTRACT

The limiting factor for actinide measurement by Accelerator Mass Spectrometry (AMS) at the Vienna Environmental Research Accelerator (VERA) is the total detection efficiency (TDE, sample to particle detector), which is strongly dependent on the ionization yield (IY) for anions in the ion source. Normally, uranium is extracted as UO^- , which results in an IY of about 10^{-3} . Fluorine-rich molecules with exceptionally high electron affinity produce strong anion currents by Cs-sputtering in the presence of excess fluorine reactants like PbF_2 . Besides providing lower detection limits, higher ion currents and ionization yields would also allow for significantly higher sample throughput. This is especially advantageous for analyses for external users, e.g. in the framework of the RADIATE Transnational Access program. Previous research suggested exploring UF_5^- extraction from metal U mixed with PbF_2 powder.

At VERA we investigated how much PbF_2 admixture would maximize U-fluoride anion extraction from a Fe_2O_3 binder with embedded traces of U-oxides. Three materials based on Vienna-KkU - each mixed with PbF_2 in variable ratios - were tested.

- I. Vienna-KkU-D30
- II. Fe solution ($\sim 200 \mu\text{g}$ Fe per sample, U:Fe = 1:30, weight ratio) added to Vienna-KkU solution and dried up, followed by calcination.
- III. Co-precipitation of UF_4 (Vienna-KkU solution) with NdF_3 (U:Nd = 1:18, weight ratio).

For "Vienna-KkU-D30", the in-house U standard Vienna-KkU was co-precipitated with Fe-hydroxide and calcined to U-oxide in Fe_2O_3 (U:Fe = 1:30, weight ratio). This material, is representative for environmental samples.

UO_mF_n^- formation from each mixture and its IY was analyzed using one of VERA's low-energy mass separators. The TDE of U, isotope ratios $^{236}\text{U}/^{238}\text{U}$, $^{233}\text{U}/^{238}\text{U}$ and the fingerprint $^{233}\text{U}/^{236}\text{U}$ of all mixtures were determined using the AMS set-up at VERA.

UF_5^- was the most efficiently extracted UO_mF_n^- ion for all the mixtures but the absolute IY for UF_5^- was limited by competing UO_mF_n^- ions in U-oxide based materials. The optimal mixing ratio of Vienna-KkU-D30 powder with PbF_2 (I.) was 1:9 by weight ratio. It showed five times higher TDE for U than optimal UO^- extraction. Individually dried and calcined material (II.) with PbF_2 showed a TDE more than three-fold higher than UO^- extraction. The UF_4 based mixture (III.) showed a TDE of up to ten-fold compared to UO^- , however, individual sub-milligram NdF_3 preparation was not yet successful. Methods I.-III. were checked for reproducibility by comparing the isotope ratios of all the mixtures to the Vienna-KkU consensus value. Materials I and II (both U-oxides) showed $^{236}\text{U}/^{238}\text{U}$ within 1- σ of Vienna-KkU. Samples prepared as UF_4 (III.) showed surprisingly high $^{236}\text{U}/^{238}\text{U}$, which might be explained by reagent contamination.

To validate method II. a typical example of an environmental sample, namely an aliquot of an air filter sample was used. This material was analyzed previously as UO^- . The $^{236}\text{U}/^{238}\text{U}$ ratios using UF_5^- extraction were in good agreement Applying UF_5^- as

molecular ion to AMS also indicated no detectable hydride background even at lower He stripper gas pressures than used for UO^- .

1. Introduction

The predominantly anthropogenic trace isotope ^{236}U ($T_{1/2} = 2.342(4) \times 10^7$ y) is best known for its use as an environmental tracer in oceanography due to its conservative behavior in sea water enabling long-distance transport. The recently introduced ratio of $^{233}\text{U}/^{236}\text{U}$ acts as a fingerprint for radioactive emissions [Hain et al., 2020]. Thus, it is possible to distinguish between environmental reservoirs influenced by either civil nuclear activities ($^{233}\text{U}/^{236}\text{U} < 1.4 \times 10^{-2}$) or mainly by fallout from nuclear weapons testing ($^{233}\text{U}/^{236}\text{U} > 1.4 \times 10^{-2}$). The detection of ^{233}U ($T_{1/2} = 1.592(2) \times 10^5$ y) from environmental samples with abundance ratios below 10^{-12} is a challenge even for the highly sensitive method of AMS. The limiting factor is the TDE and not the suppression of neighboring isotopes [Fifield et al., 1996].

AMS is specialized in the detection of long-lived radioisotopes. It uses efficient mass filtering by bending magnets and electrostatic analyzers both before and after an accelerator. Atomic isobars can in some cases be eliminated in the negative ion source. Molecular isobars are suppressed by stripping off electrons in the Tandem accelerator. A considerable drawback of using negative ions is that the ionization process does not work as efficiently as for positive ions. Moreover, it is not entirely clear which effects mainly influence anion formation [Middleton et al., 1989]. In cesium sputter sources, such as the MC-SNICS used on VERA, one commonly discussed effect is surface ionization assisted by a Cs monolayer, where the most important quantity is the electron affinity E_A of a molecule or atom to be extracted [Brown et al., 2004]. Another prominent effect is resonant electron transfer (RET) in a plasma in front of the sputter target, proposed by [Vogel et al., 2015].

One strategy to increase the IY is to prepare the sample, or the carrier (also often referred to as binder) needed for the handling, with the isotope in question as molecule with a high E_A . Most commonly, oxide molecules are used, if no interferences from molecular isobars were identified. Other strategies to improve the IY include changing the cathode geometry [Hlavenka et al., 2017], or the sputter ion source geometry or sputter ion (Xe^+ instead of Cs^+) [Ishikawa et al., 1992].

So called “superhalogens” [Gutsev et al., 1981] possess higher E_A than Cl^- with 3.61 eV [Bartmess et al., 2020]. They are characterized by the formula $\text{MF}_{(k+1)}^-$, where k is the valence of the element M . [Zhao et al., 2010] explored the formation of superhalogens throughout the periodic table. In the case of U, they extracted predominantly UF_5^- and UF_6^- ion currents from pure U metal powder mixed with PbF_2 . In addition, [Cornett et al. 2015] showed optimal mixing ratios of a NdF_3 carrier to PbF_2 in the range of 1:6 to 1:8 to efficiently extract Am and Pu fluoride molecules. Both [Zhao et al., 2010] and [Cornett et al. 2015] indicate that superhalogen ions can be efficiently extracted in sputter sources as long as an excess of F, provided by PbF_2 , was present in the AMS sample. This indicates that high mixing ratios are necessary for efficient U fluoride ion formation from U-oxide matrices.

For the analysis of trace amounts of U in environmental samples, U is usually prepared as oxides (UO_3 or U_3O_8) embedded in about 3 mg of Fe_2O_3 after a chemical purification to remove the sample matrix. 2-3 mg Fe are needed during the co-precipitation of U in

Fe(OH)₃ to ensure optimal transfer yield into the solid fraction [Qiao et al., 2015]. U does not readily form stable atomic U⁻ anions, most likely due to its low $E_A \leq 0.31$ eV [Tang et al., 2021]. AMS measurements using UO⁻ suffer from IYs of about 10⁻³ limiting the overall achievable detection efficiency [Fifield et al., 1996]. This leads to low counting statistics on especially rare isotopes like ²³³U. Moreover, ²³⁸UO⁻ extraction at VERA shows a long characteristic time interval of 30 minutes to reach desired ion currents of several nA.

The work outlined in this report had five main objectives:

1. Identify the most efficiently produced negatively charged UO_mF_n⁻ molecules formed in a Cs sputter ion source from three different sputter matrices mixed with PbF₂ (section 2.1).
2. Find the optimal mixing ratio of the sample material and PbF₂ to aid the formation of UF₅⁻, turning out to be the most prolific UO_mF_n⁻ molecule (Section 3.1).
3. Determine the TDE and the trace isotope ratios (²³⁶U/²³⁸U and ²³³U/²³⁸U), as well as assessing the suitability of three sample preparation procedures including PbF₂ admixture (section 3.2).
4. Validate the method to individually dry and calcine sub-milligram amounts of U and Fe in solution, by comparing trace isotope ratios of an environmental sample measured by UF₅⁻ extraction to ²³⁶U/²³⁸U results known from previous measurements using UO⁻ extraction (section 3.2).
5. Study the destruction of UH when UF₅⁻ is used as molecular ion for AMS (section 3.2).

2. Materials and Methods

2.1 Sample preparation

All test samples investigated in this work were prepared using the in-house U standard Vienna-KkU [Steier et al., 2008]. Three different sputter matrices with embedded Vienna-KkU were mixed with PbF₂ powder in the weight ratios 1:1, 1:3 and 1:9 (sample material to PbF₂). Each individual sample was pressed in sample holders (“cathodes”) made from Cu as Al is suspected to form Al_kF_l⁻ clusters and therefore to substantially reduce the formation of UO_mF_n⁻ ions [Prášek et al., 2020].

The first sample material was prepared by diluting a larger amount of the in-house U standard Vienna-KkU in nitric solution containing Fe (U:Fe = 1:30) F, co-precipitation with Fe(OH)₃, and calcination at 800 °C for about 4 h. The resulting material is U-oxide (UO₃ or U₃O₈) in Fe₂O₃, and is called “Vienna-KkU-D30” in the following. The obtained U to Fe ratio resembles a typical environmental sample after the currently used preparation procedure for actinide AMS [Qiao et al., 2015]. After calcination, the material was mixed with PbF₂. The resulting mixture is called “Vienna-KkU-D30+PbF₂” (see Tab. 1).

Secondly, a preparation method was developed to replace the final co-precipitation of U with Fe(OH)₃ by drying up the nitric solution with Vienna-KkU after adding the Fe carrier to obtain the final Fe₂O₃ binder. In that way the amount of Fe carrier can be

reduced to sub-milligram amounts allowing a high mixing ratio of PbF_2 to the Fe carrier while limiting the overall mixture mass. The procedure by [\[Eigl et al. 2016\]](#) was adapted to work without gold dishes for calcination and electrostatic removal devices for the sample transfer into the sample holder. Initially, 150-200 μg Fe in 0.5 M HNO_3 solution and about 5 μg U dissolved in 4 M HNO_3 was added to 10 mL of Milli-Q H_2O inside 30 mL fluorinated ethylene propylene (FEP) vials (Fig. 1). The Fe solution is based on an iron reagent of pre-nuclear origin, to exclude any influence of global nuclear weapons fallout or civil nuclear industry. The solution was dried inside the FEP vials at 80 °C for 6-8 hours in order to obtain an Fe pellet which could be easily transferred to a quartz crucible (Fig. 3) with a 50-100 μL acetone droplet (Fig. 2). The individual pellets were then calcined at 600 °C for 2 h. Finally, 2 mg PbF_2 were added and homogenized with an antistatic spatula. This mixture was labelled “($\text{U}_{[\text{sol}]} + \text{Fe}$)+ PbF_2 ”. The sample transfer yield from the quartz crucible to the Cu sample holder was determined to be above 70% on average (see Tab. 1). After initial column separation using extraction chromatography and pre-concentration of the U fraction the environmental air filter sample and a corresponding process blank were individually dried and calcined using the method described above [\[Steier et al., 2019, Hain et al., 2022\]](#).

Thirdly, a sample material with a different approach was explored, in which U is prepared directly as a fluoride compound. Here, UF_4 was prepared by co-precipitation of U (Vienna-KkU) with NdF_3 ($\text{U}:\text{Nd} = 1:18$ by weight) using HF according to [\[Prášek et al. 2020\]](#), and dried at 50 °C under Ar atmosphere over night. This material was then mixed with PbF_2 . The mixture was labelled “($\text{UF}_4 + \text{NdF}_3$)+ PbF_2 ” (see Tab. 1). Samples from this mixture were prepared together with colleagues of CTU Prague.



Fig. 1. 30 mL FEP vial with Al foil to mitigate electrostatic charging.



Fig. 2. Transfer of the Fe-carrier pellet using a 50-100 μL droplet.



Fig. 3. Quartz crucible after sample transfer turned upside down, illustrating transfer losses.

Table 1. Mass of materials used to prepare one representative cathode per mixture. The subscript [sol] indicates mass of the element in solution. (†) indicates that the total Vienna-KkU-D30+ PbF_2 mixture mass was limited to ≥ 30 mg. (‡) The total ($\text{UF}_4 + \text{NdF}_3$)+ PbF_2 mixture mass was limited to ≥ 50 mg. The total test sample mass for optimal sputter duration was $< 3\text{mg}$

Sample of mixture	Vienna-KkU-D30 (mg)	U _[sol] (μg)	Fe _[sol] (μg)	(UF ₄ +NdF ₃) (mg)	PbF ₂ (mg)	Aliquot of total mixture per cathode (%)
Vienna-KkU-D30+PbF ₂	0.23±0.01	–	–	–	1.79±0.01	<10 (†)
(U _[sol] +Fe)+PbF ₂	–	5.7±0.2	203±6	–	1.92±0.01	100
(UF ₄ +NdF ₃)+PbF ₂	–	–	–	0.26±0.01	1.98±0.01	<6 (‡)

2.2 Recording the mass spectrum

Every mixture was investigated using a Cs sputter ion source (MC-SNICS) and one of the injector mass spectrometers at VERA. The composition of the extracted anion beam in the mass range of 240 u to 355 u was measured by ramping up the injection energy from 25 keV to 40 keV and measuring the ion currents in a Faraday cup behind a 90° bending magnet kept at constant field. The mass calibration was carried out with PbF₃[–] and Cu₅[–] clusters. Three consecutive mass spectra were acquired within ten minutes for every sample, before advancing to the next. The disk-shaped sample magazine of our ion-source accommodates up to 40 samples, and one complete rotation of the wheel is called a turn in the following. A turn was repeated until recorded ion currents dropped below a threshold of 0.1 nA.

The IY was calculated from the number of UO_mF_n[–] ions corresponding to the measured current, divided by the number of U atoms present in every cathode. The cumulative IY between samples of the same composition varied by up to a factor of 2 (see section 3.2), which is not unexpected, considering previous observations. This spread of results dominates the uncertainty, as it is much greater than the uncertainty of the U contents of each sample. The given uncertainty of the IY per mixture is the uncertainty of the mean of samples prepared from each mixture (see Table 2).

2.3 AMS using fluoride ions

The total detection efficiency (TDE) for U extracted in the form of UF₅[–] as well as the isotopic ratios ²³⁶U/²³⁸U, ²³³U/²³⁶U for the materials described in section 2.1 were investigated with the AMS setup at VERA.

A recent description of the AMS setup at VERA and the measurement routine for the detection of actinides extracted as monoxides is given in [\[Steier et al. 2019\]](#). The procedure has been adjusted to fluorides. A pilot beam of ²³⁸UF₅[–] anions was injected into the tandem accelerator operated at 1.65 MV. Helium gas stripping at the high voltage terminal was used. The maximum stripping yield is achieved in charge state U³⁺. The actinide detection beam line was tuned with ²³⁵U³⁺ extracted as ²³⁵UF₅[–] from metallic Fe powder (Merck) mixed with PbF₂ 1:9 by weight. The trace isotope ions ²³⁶U³⁺ and ²³³U³⁺ were sequentially injected and identified in a Bragg-type gas ionization chamber via pulse height and width analysis.

The TDE of U was calculated by the ratio of the number of $^{238}\text{U}^{3+}$ ions detected, divided by ^{238}U present in each sample. As with the IY results, the TDE data for samples of the same mixture showed a significant spread and was therefore averaged. The uncertainty of the results given is the standard deviation of the samples prepared from each mixture. The isotopic ratios $^{236}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{236}\text{U}$ were calculated from the detected count rates of $^{233}\text{U}^{3+}$ and $^{236}\text{U}^{3+}$ in the ionization chamber and the $^{238}\text{U}^{3+}$ current.

In addition, the destruction of $^{238}\text{U}^{3+}$ was studied by selecting mass 334 u at the low-energy side ($^{238}\text{UHF}_5^-$ or $^{239}\text{PuF}_5^-$) and injecting it into the accelerator. Mass $^{239}\text{U}^{3+}$ was analyzed at two different He stripper gas pressures to assess the $^{235}\text{U}^{3+}$ background for $^{236}\text{U}^{3+}$ after the accelerator [Lachner et al., 2013]. The mass $^{239}\text{U}^{3+}$ events ("m239 $^{3+}$ ") were compared to the $^{238}\text{U}^{3+}$ current at the standard He stripper pressure of 1 Pa for UO^- measurements. The second He stripper gas pressure was 0.4 Pa, where the maximum stripping yield for U^{3+} ions is achieved. The investigated mixtures were Vienna-KkU-D30+ PbF_2 (see table 1) and pure Vienna-KkU, also mixed 1:9 with PbF_2 . Results are shown in table 4.

3. RESULTS AND DISCUSSION

3.1 Formation of UO_mF_n^- ions

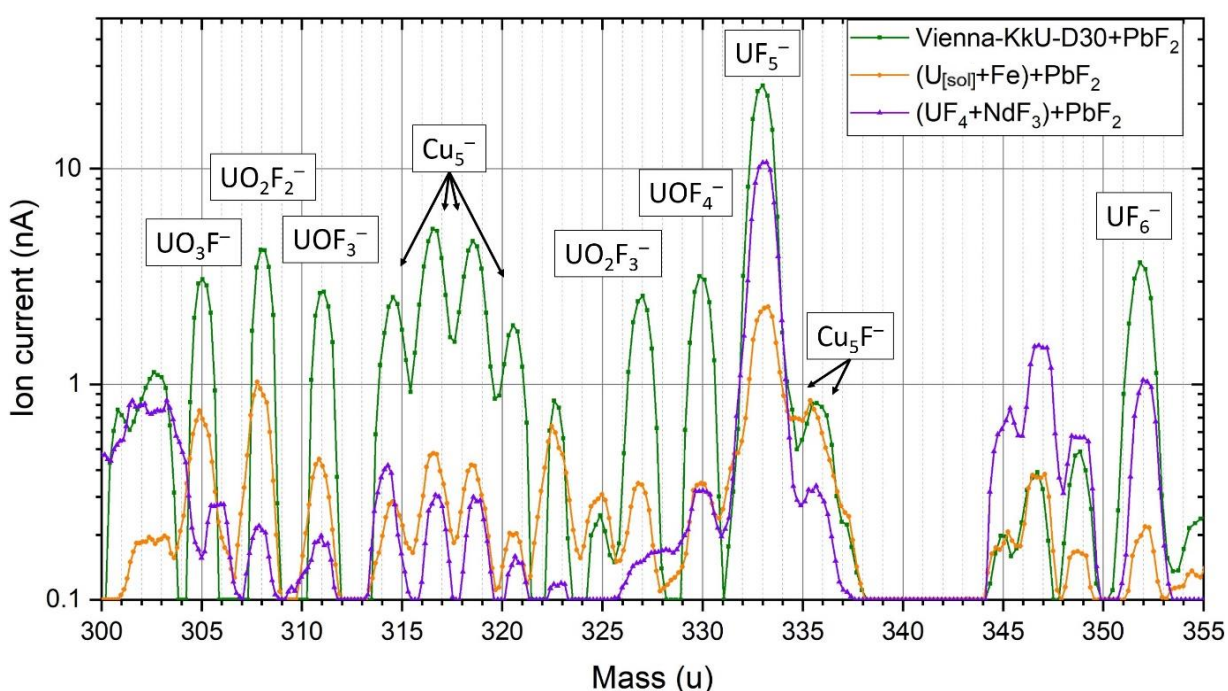


Figure 4. Ion currents measured in a Faraday cup vs. mass. Colors indicate the three investigated mixtures. UO_mF_n^- molecules were only found in the shown mass range.

Figure 4 shows the ion current vs. mass extracted from samples of three mixtures with PbF_2 in the mass range of 300 u to 355 u. The following UO_mF_n^- molecules were clearly identified in the recorded mass spectrum (see Fig. 4): UO_3F^- , UO_2F_2^- , UOF_3^- , UO_2F_3^- , UOF_4^- , UF_5^- and UF_6^- , with UF_5^- generating the highest ion current of several tens of nA. The mass region from 240 u to 300 u only showed peaks of Cu_4^- and PbF_k^- ions

and the corresponding mass range is therefore not presented. The spectrum shown was taken in the 4th turn, after the first 30 minutes of measurement on each sample. UF_5^- produced the strongest ion currents of all UO_mF_n^- molecules extracted from each of the mixtures. The highest UF_5^- ion currents (ca. 30 nA) were extracted at the beginning of the measurement and continuously declined thereafter. This behavior was independent of the sputtered mixture. The ion current extracted from $(\text{UF}_4+\text{NdF}_3)+\text{PbF}_2$ did not show significant formation of other UO_mF_n^- molecules, whereas mixtures containing U as oxides (green and orange) showed more than a factor of 10 higher formation of other UO_mF_n^- ion currents.

Among all UO_mF_n^- molecules the IY of UF_5^- was the highest. The PbF_2 mixing ratio that resulted in the highest UF_5^- IY was always 1:9 by weight. Both mixtures with U-oxide showed competing currents of UO_3F^- , UO_2F_2^- and UOF_3^- with 65–70% intensity relative to UF_5^- , which certainly limits the UF_5^- IY. The mixture $(\text{UF}_4+\text{NdF}_3)+\text{PbF}_2$ on the other hand showed no substantial current of U-containing ions other than UF_5^- .

Based on data from Cu sample holders filled with PbF_2 the background of $^{63}\text{Cu}_5\text{F}^-$ (333.65 u) for the neighboring UF_5^- (333.04 u) was estimated at 10%. The presented IY data was corrected accordingly.

Table 2. UF_5^- ionization yield for the explored mixtures and 1σ uncertainties.

Mixture	UF_5^- ionization yield (%)
Vienna-KkU-D30+ PbF_2	2.49 ± 0.12
$(\text{U}_{[\text{sol}]}+\text{Fe})+\text{PbF}_2$	1.30 ± 0.45
$(\text{UF}_4+\text{NdF}_3)+\text{PbF}_2$	3.40 ± 0.30

The UF_5^- IYs are given in table 2. Tests showed transfer losses in the range of 20-35% from quartz crucible to sample holder (see Figure 3). The results for the small $(\text{U}_{[\text{sol}]}+\text{Fe})+\text{PbF}_2$ samples in turn are the most realistic proxy for the IY of environmental samples. The IY of UF_5^- for the given mixtures (Tab. 2) shows a 5 to 10-fold improvement compared to UO^- extraction. In addition, more than 90% of the total extracted U was recorded within 2 h from the start of the measurement. This rapid extraction has the potential to significantly speed up routine AMS measurements for U analysis.

3.2 Results for the application of fluorides in AMS

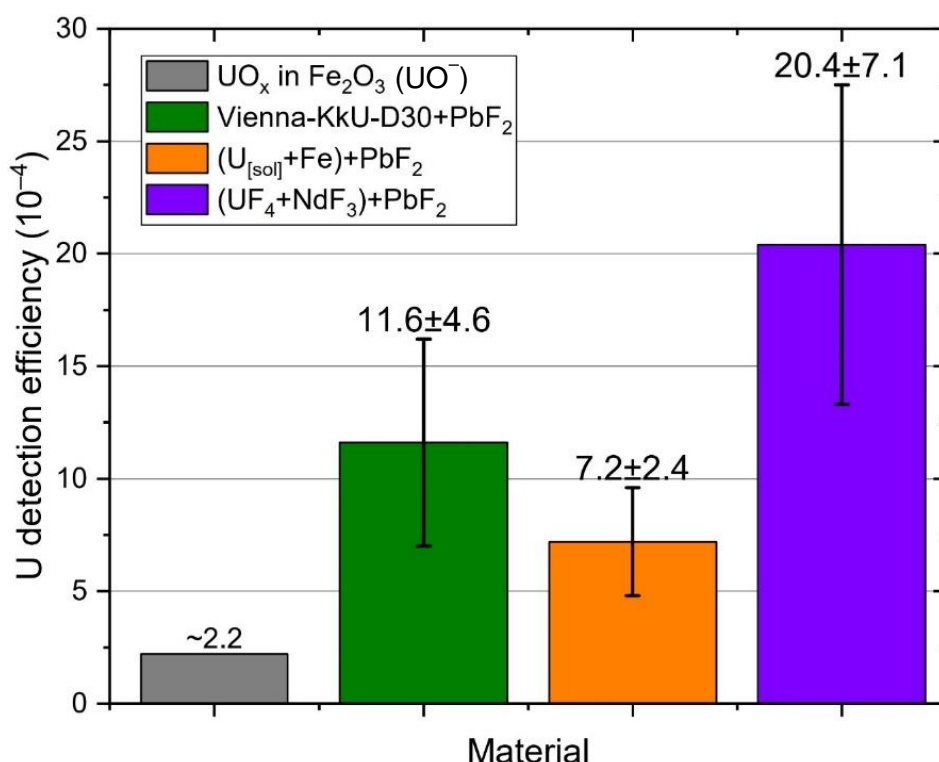


Figure 5. Total detection efficiencies of U by UF_5^- extraction of the three investigated mixtures is shown with 1σ error bars. The detection efficiency by UO^- extraction at VERA is given in grey for comparison [Eigl et al., 2016].

In figure 5 the TDE for U of each of the mixtures Vienna-KkU-D30+ PbF_2 , $(\text{U}_{[\text{sol}]} + \text{Fe}) + \text{PbF}_2$ and $(\text{UF}_4 + \text{NdF}_3) + \text{PbF}_2$ is shown relative UO^- extraction. The bars show the statistical uncertainty of the TDE over the course of one AMS measurement. For the present work the UF_5^- ion source output was set very low to avoid rapid sputtering and hence, consumption of the investigated targets which would have prevented verification of the reproducibility of the results.

Uranium extraction from Vienna-KkU-D30+ PbF_2 as UF_5^- and subsequent detection as U^{3+} was on average five times as efficient as the maximum obtained with UO^- extraction at VERA. The detection efficiency achieved with individually dried sub-milligram samples still more than tripled compared with that obtained with UO^- . The difference in TDE between Vienna-KkU-D30+ PbF_2 and $(\text{U}_{[\text{sol}]} + \text{Fe}) + \text{PbF}_2$ can be explained by transfer losses after the calcination step (see Fig. 3) due to electrostatic charging and material sticking to the quartz crucible. By using the later developed drying method for the mixture $(\text{U}_{[\text{sol}]} + \text{Fe}) + \text{PbF}_2$ the same improvement in TDE should be achievable for environmental samples.

The mixture $(\text{UF}_4 + \text{NdF}_3) + \text{PbF}_2$ provided an average TDE of U extracted as UF_5^- of $(20.4 \pm 7.1) \times 10^{-4}$. Co-precipitation of U with the fluorinated carrier UF_4 doubled the detection efficiency of U extracted as UF_5^- relative to Vienna-KkU-D30+ PbF_2 . This increase can be explained by the reduction of the formation of competing UO_mF_n^- molecules. Unfortunately, first attempts to prepare individual sub-milligram carrier samples with the method of [Prášek et al. 2020] failed.

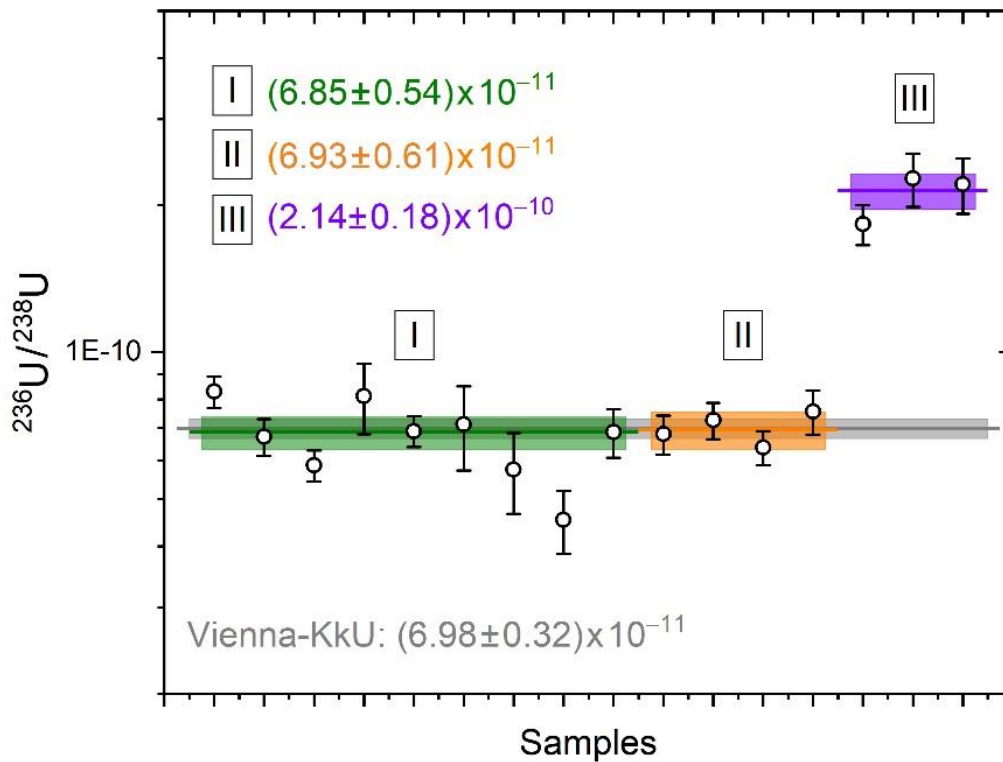


Figure 6. $^{236}\text{U}/^{238}\text{U}$ results per cathode with corresponding 1σ error bars. Averages for each mixture are shown by the dark lines, light colored bars indicate uncertainties. The Vienna-KkU consensus ratio is indicated in grey [Steier et al., 2008].

AMS results on the isotope ratio $^{236}\text{U}/^{238}\text{U}$ for the investigated mixtures are shown in Figure 6. The individual samples of each mixture are combined into groups. All the prepared samples from the three mixtures were expected to agree within their $^{236}\text{U}/^{238}\text{U}$ ratio as they were prepared from Vienna-KkU and only differ by the applied preparation method.

Both Vienna-KkU-D30+PbF₂ and (U_[sol]+Fe)+PbF₂ showed an average $^{236}\text{U}/^{238}\text{U}$ ratio in very good agreement with the Vienna-KkU consensus ratio $^{236}\text{U}/^{238}\text{U} = (6.98 \pm 0.32) \times 10^{-11}$ within their respective 1σ uncertainty. On the other hand, the mixture (UF₄+NdF₃)+PbF₂ showed a ratio of $^{236}\text{U}/^{238}\text{U} = (2.14 \pm 0.18) \times 10^{-10}$, which is significantly too high. This indicates a uranium contamination with a $^{236}\text{U}/^{238}\text{U}$ ratio higher than that of Vienna-KkU.

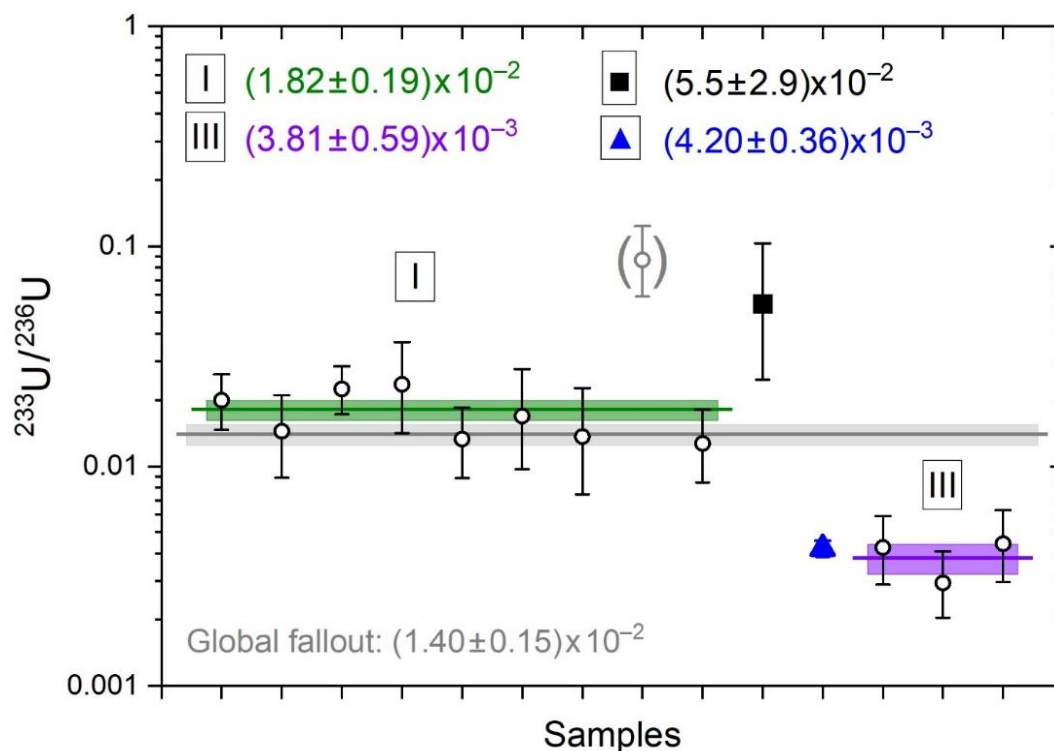


Figure 8. $^{233}\text{U}/^{236}\text{U}$ ratio with 1- σ error bars of Vienna-KkU-D30 samples prepared using method I and III, the air filter sample and the process blank. Low $^{233}\text{U}/^{236}\text{U}$ data of samples prepared by method III. and the air filter sample (\blacktriangle) indicate influence of civil nuclear industry. Samples prepared by method I. show ratios similar to global fallout as well as the process blank (\blacksquare). The $^{233}\text{U}/^{236}\text{U}$ ratio representing global fallout by [Hain et al., 2020] is indicated in grey.

The $^{233}\text{U}/^{236}\text{U}$ isotopic ratio, recently introduced as a fingerprint distinguishing anthropogenic uranium from global fallout of nuclear weapons tests and reactor material was analyzed in all samples [Hain et al., 2020]. The corresponding measurement results are given in figure 8. The average $^{233}\text{U}/^{236}\text{U}$ ratio of Vienna-KkU-D30+PbF₂, i.e. group I, is $(1.82 \pm 0.19) \times 10^{-2}$ which is within 1.4 σ of the global fallout ratio at $(1.40 \pm 0.15) \times 10^{-2}$. However, this is no indication of global fallout influence in the material, which was already separated before 1918 from ore from Jachymov, Czech Republic. More likely, it results from natural ^{233}U production in high-grade ore, as already observed by [Peppard et al. 1952]. A considerably lower ratio $^{233}\text{U}/^{236}\text{U}$ was found in the mixture (UF₄+NdF₃)+PbF₂, i.e. group III. The $^{233}\text{U}/^{236}\text{U}$ ratio was $(3.81 \pm 0.59) \times 10^{-3}$. Lower $^{233}\text{U}/^{236}\text{U}$ ratio indicate influence of material released by civil nuclear industry. This may be explained by the fact that the Nd₂O₃ used for UF₄+NdF₃ co-precipitation originates from a lab with ample experience in analyses for civil nuclear industry. The $^{233}\text{U}/^{236}\text{U}$ ratio of the air filter sample also shows the signature of spent nuclear fuel. The process blank displays a significantly higher $^{233}\text{U}/^{236}\text{U}$ ratio corresponding to global fallout influence, however, at very low concentration of both isotopes.

Table 3. Results for the investigated air filter sample and process blank extracted as UF_5^- compared to the results using UO^- .

Sample (extracted as)	Avg. ^{238}U current (pA)	Avg. ^{236}U count rate (cps)	Avg. ^{233}U count rate (cps)	$^{236}\text{U}/^{238}\text{U}$
Air filter sample (UF_5^-)	1.22	5.317 ± 0.061	$(2.35 \pm 0.17) \times 10^{-4}$	$(1.561 \pm 0.018) \times 10^{-6}$
Air filter sample (UO^-)	0.17	0.58 ± 0.23	–	$(1.48 \pm 0.14) \times 10^{-6}$
Process blank (UF_5^-)	0.24	$(1.33 \pm 0.31) \times 10^{-2}$	$(7.17 \pm 3.2) \times 10^{-4}$	$(2.44 \pm 0.58) \times 10^{-8}$
Process blank (UO^-)	0.023	$(3.3 \pm 1.9) \times 10^{-2}$	–	$(8.25 \pm 4.6) \times 10^{-8}$

The results of the air filter sample, obtained with UO^- and UF_5^- extraction, are shown in table 3. The $^{236}\text{U}/^{238}\text{U}$ ratio of the air filter sample could be reproduced within 1σ uncertainty. Moreover, the uncertainty obtained by UF_5^- extraction is significantly smaller than previously achieved by UO^- extraction. However, this is not only an effect of the higher ionization yield, but also the air filter sample mass was 9 times higher for the UF_5^- extraction compared to UO^- in this first experiment.

Table 4. Results on UH destruction at two different He stripper gas pressures for two mixtures containing Vienna-KkU extracted as UF_5^- together with data on UO^- from [Steier et al 2019].

Sample (extracted as)	He stripper pressure (Pa)	Avg. $^{238}\text{U}^{3+}$ current (nA)	Avg. $m^{239}\text{U}^{3+}$ count rate (cps)	$m^{239}\text{U}^{3+} / ^{238}\text{U}^{3+}$ (10^{-12})
Vienna-KkU-D30 + PbF_2 (UF_5^-)	1.0	0.43 ± 0.16	$(1.03 \pm 0.28) \times 10^{-2}$	(8.5 ± 2.0)
Vienna-KkU-D30 + PbF_2 (UF_5^-)	0.4	0.69 ± 0.19	$(1.19 \pm 0.64) \times 10^{-2}$	(6.6 ± 1.7)
Vienna-KkU + PbF_2 (UF_5^-)	1.0	50 ± 3.2	0.67 ± 0.15	(3.0 ± 2.2)
Vienna-KkU + PbF_2 (UF_5^-)	0.4	97 ± 13	0.78 ± 0.15	(3.1 ± 2.8)
Vienna-KkU (UO^-)	1.0	~ 200	$\sim 10^{-2}$	$\sim 10^{-2}$
Vienna-KkU (UO^-)	0.4	~ 200	~ 200	~ 50

Furthermore, the destruction of $^{238}\text{UH}^{3+}$ to assess the $^{235}\text{U}^{3+}$ background for measurements of ^{236}U using UF_5^- extraction was studied. Hence, mass 334 u ($^{238}\text{UHF}_5^-$ or $^{239}\text{PuF}_5^-$) was injected to the accelerator. Mass $^{239}\text{U}^{3+}$ was analyzed relative to the $^{238}\text{U}^{3+}$ current. Table 4 shows the results.

The measured count rates and the resulting $m^{239}\text{U}^{3+} / ^{238}\text{U}^{3+}$ ratio for the two Vienna-KkU mixtures did not change significantly when decreasing the He stripper gas pressure from 1 Pa to 0.4 Pa. The $m^{239}\text{U}^{3+} / ^{238}\text{U}^{3+}$ ratios of both mixtures with PbF_2 strongly indicate the presence of real ^{239}Pu , probably in the reagents or the sample holder. $^{238}\text{UH}^{3+}$ would have been strongly reduced by an increase in He pressure. In addition, the $m^{239}\text{U}^{3+} / ^{238}\text{U}^{3+}$ ratios by UF_5^- extraction of Vienna-KkU mixtures are comparable despite of roughly 30 times more U content in the pure Vienna-KkU.

Moreover, the $m239^{3+} / ^{238}\text{U}^{3+}$ ratio of both Vienna-KkU mixtures with PbF_2 at 1 Pa stripper pressure showed about two orders of magnitude higher ratios of $m239^{3+} / ^{238}\text{U}^{3+}$ relative to the previous UO^- data [Steier et al., 2019]. However, with a He stripper gas pressure of 0.4 Pa, both UF_5^- extracted mixtures showed an order of magnitude lower $m239^{3+} / ^{238}\text{U}^{3+}$ ratio compared to Vienna-KkU extracted as oxide. This indicates that $^{238}\text{UH}^{3+}$ ions produce less background when U is extracted as UF_5^- compared to UO^- . The high current observed in [Steier et al., 2019] for UO^- (table 4) can be explained by the fact that this sample was several mg of pure U-oxide, while for Vienna-KkU+ PbF_2 , the uranium oxide is diluted 1:9 with PbF_2 . Thus, the concentration in the fluoride mixture is ten times lower. However, for environmental samples, mg amounts of uranium will usually not be available.

4. CONCLUSIONS AND OUTLOOK

Three different sample preparation methods using PbF_2 admixture for efficient U analysis by AMS were systematically investigated at VERA. The formation of UO_mF_n^- ions and the isotope ratios $^{236}\text{U}/^{238}\text{U}$, $^{233}\text{U}/^{236}\text{U}$ were measured and validated with the Vienna-KkU standard.

The $^{236}\text{U}/^{238}\text{U}$ isotope ratios of U-oxide-based mixtures agreed with the Vienna-KkU consensus, whereas the $^{236}\text{U}/^{238}\text{U}$ ratios of first U-fluoride-based materials were significantly higher. The application of the $^{233}\text{U}/^{236}\text{U}$ isotopic ratio as fingerprint suggests that the neodymium reagent used to produce the $(\text{UF}_4+\text{NdF}_3)+\text{PbF}_2$ material may have been influenced by contamination from nuclear fuel.

A new sub-milligram Fe preparation method limiting the overall sample size while allowing high PbF_2 mixing ratios (1:9 and above) was developed. The $^{236}\text{U}/^{238}\text{U}$ isotope ratios of an environmental air filter sample could reproduce the ratios previously measured using UO^- extraction.

The presented results show the suitability of UF_5^- as molecular anion for AMS applications. UF_5^- was the most efficiently formed UO_mF_n^- anion from samples containing U as oxides by admixture of PbF_2 (1:9 by weight). The extraction of UF_5^- was 3 to 5-fold as efficient compared to UO^- . Changing the chemistry to co-precipitating UF_4 with NdF_3 even leads to a 10-fold improvement of detection efficiency compared to UO^- extraction. Moreover, UF_5^- extraction reduces the time to sputter 90% of the sample to less than 2 h compared to 4-5 h for UO^- .

Applying UF_5^- as molecular ion to AMS also indicated less hydride background even at lower He stripper gas pressures than used for UO^- .

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