

# AMS on the actinides in spent nuclear fuel

a study on a technique for inventory measurements

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### Sammanfattning

Denna rapport handlar om huruvida Accelerator masspektrometri (AMS) är en lämplig teknik för mätning av aktinidinventariet i använt kärnbränsle. Rapporten går också igenom om AMS är bättre än nuvarande tekniker för dessa mätningar. AMS är en typ av masspektrometri (MS) och har en mängd användningsområden, kol-14 metoden är en av de vanligaste. AMS har också ofta använts för att göra mätningar på aktinid innehåll i biomassa som kan ha varit i kontakt med vapenplutonium, och i närheten av anrikningsanläggningar och upparbetningsanläggningar. Det visas i rapporten att AMS är en mer känslig metod än de nuvarande teknikerna som används för mätningar på aktinidinventariet i använt kärnbränsle. ICP-MS är den aktuella teknik som används för mätningar på aktinidinventariet i använt kärnbränsle vid Svenska Kärnbränslehantering AB (SKB). ICP-MS är också en typ av MS teknik. MS är väl beprövad för mätningar av inventariet på använt kärnbränsle. Skillnaden i känslighet varierar i flera storleksordningar beroende på vilken isotop som är intressant för mätningarna. Den lägre detektionsgränsen för AMS är cirka  $10^5$ - $10^7$  atomer, vilket gör det möjligt att använda prover från kärnbränsle som är i storleksordningen  $10^{-10}$ - $10^{-16}$  g för att uppnå den lägre detektionsgränsen. Rekommendationen från denna rapport är att göra undersökningar om AMS också är ekonomiskt lönsam och tillräckligt effektiv teknik för framtida bruk inom mätningar av aktinidinventariet i använt kärnbränsle.

### Abstract

This report is concerned with the question whether Accelerator mass spectrometry (AMS) is a suitable technique for measuring actinide inventory in spent nuclear fuel, and if it is better than present techniques for these measurements. AMS is a kind of Mass spectrometry (MS) and has a lot of applications where radio carbon dating is one of the most common. AMS has been used for making measurements on actinides before but mostly from traces in bioassay that could have been in contact with weapon plutonium, and in bioassay near enrichment plants and reprocessing plants. It is shown in this report that AMS is more sensitive in low level measurements than the current technique for spent nuclear fuel. ICP-MS is the current technique in use for inventory measurements on nuclear fuel at Swedish Nuclear Fuel and Waste Management Company (SKB). ICP-MS is also a kind of MS technique which is well-tried for inventory measurements on spent nuclear fuel. The difference in sensitivity ranges in levels of magnitude depending on which isotope that is interesting for measurements. The lower detection limits for AMS is about  $10^5$ - $10^7$  atoms which makes it possible to use samples from nuclear fuel that is in the order of  $10^{-10}$ - $10^{-16}$  g to achieve the lower detection limit. The recommendation from this report is to make studies if AMS also is an economical and efficiently suitable technique for future use on the actinide inventory in spent nuclear fuel.

Bachelor thesis

AMS on the actinides in spent nuclear fuel, a study on a technique for inventory measurements

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## **1. Project introduction**

The idea of this project is to make an evaluation whether accelerator mass spectrometry (AMS) is a competitive technique to measure the actinide inventory of used nuclear fuel compared with present techniques. To determine that, features and sensitivities of the two techniques will be compared. Another purpose is to point out which of the actinides are emitting neutrons due to spontaneous fission and why accurate data on them is needed. Then there is also an interest to know how the inventory of actinides in used nuclear fuel is composed.

Examples on the present measuring techniques are for example Thermal Ionization Mass Spectrometry (TIMS), High Performance Liquid Chromatography (HPLC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The TIMS is an accurate method but it is very time consuming. The HPLC and the ICP-MS are less accurate, but they are useful when measuring larger samples [1]. The combined ICP-MS and HPLC-method is the present method used by the staff at SKB for measuring inventory in used nuclear fuel [2]. More about this method can be read about later in this report. To make an approximate determination of the fuel inventory one can use codes such as CASMO, ORIGEN and HELIOS [1] [2]. These codes make calculations of the fuel inventory.

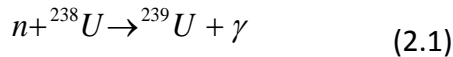
Some of the actinides isotopes are present only in small concentrations in used nuclear fuel, but they still need considered due to their neutron emissions. An accurate measurement technique is needed to measure the content of these isotopes. A technique which has the ability to make measurements on small sample sizes with high accuracy is Accelerator mass spectrometry (AMS). A description of how AMS works will be found later in this report.

## **2. Composition of spent nuclear fuel**

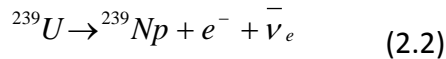
As mentioned in the introduction, composition of nuclear fuel can be determined by different codes. In this report a calculation from a report from SKB will be used as an example [5]. The actinide composition of boiling water reactor (BWR) fuel from computations is shown in table A1 in the appendix. The computations are on one ton of fresh uranium fuel to a burn rate of 55MWd/kg directly put out of the reactor. In table A2 in the appendix, about the same is displayed for pressure water reactor (PWR) fuel, but the focus in this report is on the BWR case. The composition is calculated with a combination of different codes including CASMO.

Tables A1 and A2 in the appendix show that when the nuclear fuel is fresh, it has an approximate composition of about 96.7%  $^{238}\text{U}$  about 3.3%  $^{235}\text{U}$  and a negligible amount of  $^{234}\text{U}$ . These values are valid for both of the fuel types. When the fuel has been used to a burn out rate of about 55MWd/kg for the BWR case, a lot of new isotopes have been produced. The most common isotope is still  $^{238}\text{U}$ , but then there is only about 0.2% of  $^{235}\text{U}$ . The most common of the new isotopes is  $^{239}\text{Pu}$  with abundance of 0.43% and  $^{236}\text{U}$  with about 0.47%. The rest of the isotopes have less abundance than  $^{235}\text{U}$ . The case is similar for the PWR fuel.

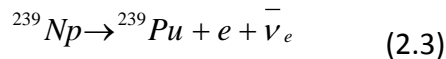
In a nuclear reactor, the fuel is bombarded with neutrons which  $^{235}\text{U}$  may absorb and undergo a fission, which means that it splits into two lighter nucleuses such as Krypton and Barium. But when  $^{238}\text{U}$  captures a neutron the following reaction is common:



${}^{239}\text{U}$  is a radioactive isotope with a half-life of approximate two hours and beta decays into  ${}^{239}\text{Np}$ :



In turn  ${}^{239}\text{Np}$  has a half-life in the order of two days, it beta decays into Pu239:



${}^{239}\text{Pu}$  has a half-life of about 24000 years. It has larger fission cross section than  ${}^{235}\text{U}$  which make it much more probable for  ${}^{239}\text{Pu}$  to absorb a neutron than for  ${}^{235}\text{U}$  [3]. Because  ${}^{239}\text{Pu}$  has a relatively long half-life, there will be a lot of time to capture new neutrons in the reactor and build up heavier isotopes of Plutonium.  ${}^{240}\text{Pu}$  is undesirable in nuclear waste management, because it has a large probability of spontaneous fission. The problems with spontaneous fission will be discussed in chapter 3.  ${}^{240}\text{Pu}$  may capture another neutron and become  ${}^{241}\text{Pu}$  which is also fissionable, which could also capture a neutron and become  ${}^{242}\text{Pu}$ .  ${}^{242}\text{Pu}$  has also a large probability of spontaneous fission.  ${}^{241}\text{Pu}$  decays with beta decay with a half-life of about 14 years [3] into  ${}^{241}\text{Am}$ .  ${}^{241}\text{Am}$  may in its turn capture even more neutrons, build up heavier isotopes and after a few more of these reactions it is possible to have for example  ${}^{242}\text{Cm}$ ,  ${}^{244}\text{Cm}$  and  ${}^{246}\text{Cm}$  in the fuel, more details is shown in figure 1. Like  ${}^{240}\text{Pu}$  and  ${}^{242}\text{Pu}$ ,  ${}^{242}\text{Cm}$ ,  ${}^{244}\text{Cm}$  and  ${}^{246}\text{Cm}$  have a relatively high probability of spontaneous fission. The build-up of these isotopes is possible because of the relatively long half-life of  ${}^{241}\text{Am}$ , which is around 430 years [3]. Some of the transmutation paths can be seen in Figure 1 below.

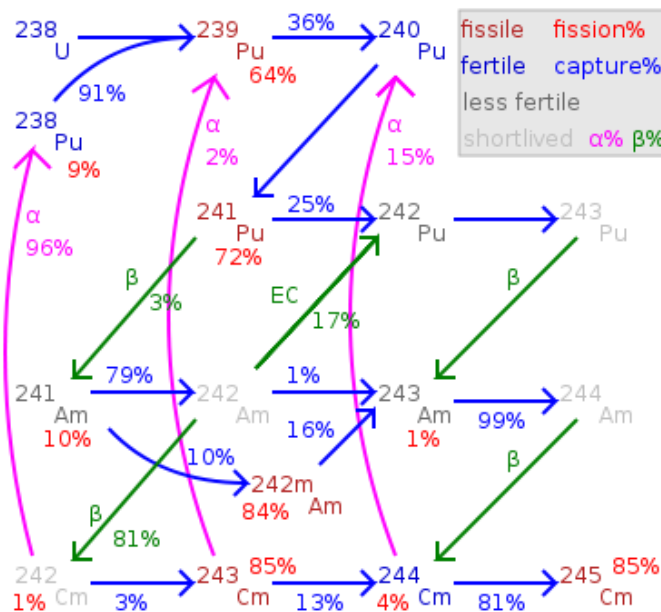


Figure 1- transmutation paths for actinides in a light water reactor [4]

### 3. Spontaneous fission (SF) and neutron emissions

Ionizing radiation has enough energy to as the name suggests ionize atoms. In large doses, ionized radiation can worst cases damage cells in the body [6]. There are different kinds of ionizing radiation. A few examples are alpha, beta, neutron and gamma radiation. Neutron radiation is harder to shield against compared with beta and alpha radiation because it has no electric charge.

When the reactor is turned off, the induced fission stops, but there are still isotopes that can undergo spontaneous fission. Depending on the quantities and SF rate (number of SFs per decay) of a specific isotope, there are still two or three neutrons that are emitted at each fission [7]. In a reactor, spontaneous fission generates more neutrons to react, but it is undesirable when handling radiation protection after the fuel is taken out of the reactor. The spontaneous fission does also produce radioactive isotopes and does also keep the fuel warm which could be a material issue when it comes to handling the fuel waste.  $^{239}\text{Pu}$  is a great fuel in the reactor, because it has high probabilities to fission, but when it comes to waste management, this property combined with spontaneous fission gives a source of more neutrons. Normally if  $^{239}\text{Pu}$  absorbs a neutron, more than one neutrons are produced as it fissions [7]. This report will evaluate which sources of SF that contributes the most.

To evaluate which of these isotopes which are the most interesting to measure on these conditions, calculations of the number of fissions per second have to be made. To do this the values in table A1 will be used. To calculate how many SFs there are per second, the activity of the isotopes in the samples has to be known. To calculate the activity, the decay constant and the number of atoms has to be known. Equation (3.1) shows how to calculate the number of atoms:

$$N = \frac{m}{M} \cdot N_A \quad (3.1)$$

In this equation N is the number of atoms, m is the total mass of the isotope of interest, M is the molar mass and  $N_A$  is Avogadro's number. By putting in the values of the masses and molar masses from table A1 to (3.1) the number of atoms of a specific isotope can be acquired. To calculate the activity, the decay constant  $\lambda$  is also required. By putting in the different half-lives from table A3,  $\lambda$  can be calculated[8]:

$$\lambda = \frac{\ln 2}{t_{1/2}} \quad (3.2)$$

where  $t_{1/2}$  is the half-life of the isotope. The activity may then be calculated from the following formula:

$$n = \lambda N \quad (3.3)$$

Where n is the activity. To calculate the number of SFs per second the activity is multiplied with SF-rate:

$$n_{sf} = nR_{sf} \quad (3.4)$$

Where  $n_{sf}$  is the number of SFs per second,  $n$  is the activity and  $R_{sf}$  is the SF-rate from table A3 in the appendix. When the activity is known, the  $n_{sf}$  can be calculated from (3.4). The result of the  $n_{sf}$  is presented in table A4 in the appendix.

The values from the table A4 indicates that  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{242}\text{Cm}$ ,  $^{244}\text{Cm}$  and  $^{246}\text{Cm}$  have SF activities that are at least a thousand times larger than most of the other isotopes. That it is precisely isotopes of even mass and atomic number that would be those that are most likely to SF, is likely a result of the odd-even effect. These isotopes could be the most interesting to investigate with an accurate measuring technique if they are at these levels. Due to the large abundance of  $^{238}\text{U}$ , it can be assumed that the activity from many other isotopes can be neglected, but that does not seem to be the case.

#### **4. Introduction to MS and AMS**

To understand AMS we should also look at its predecessor, the mass spectrometry (MS). The most common way to measure the actinide inventory at SKB in spent nuclear fuel at present time is a kind of MS. An MS system can be described by four steps. First, the ions are created in an ion source, then accelerated, analysed in a Mass/energy analyser and then detected by a detector [9]:

1. An ion source

One examples of an ion source is the inductively couple plasma (ICP) source, where the ions are created by an argon plasma [10]. Another example is the Thermal ionization (TI) ion source. As the name states this source ionizes the samples thermally, which can be done by letting a high electric current pass through the sample [11]. Both these methods were mentioned in the introduction.

2. Acceleration

The ions are accelerated in an electric field with energies in the kV level [12]

3. Momentum/Mass/Energy Analysis

The momentum/mass/energy analyser is a key part of the measurement. This is where the separation of elements takes place so that the isotope of interest to measure is sorted out. A momentum/mass/energy analyser can be a bending magnet, where the elements are separated by mass and kinetic energy to charge ratio. Another analyser is an electrostatic analyser, in such analyser the ions travel in an electric field and is bent of separated out by energy to charge ratio. Figure 2 displays in general how an analyzing magnet works.

A combination of the two methods above can be made, then there is both a magnetic field and an electrostatic field, this is called a velocity filter or a Wien filter, then the isotopes are separated by its mass and kinetic energy to charge ratio. One of the most commonly used is a quadrupole mass filter [13], where the elements are separated by their mass to charge ratio. A sketch of an MS with a quadrupole mass filter is displayed in figure 3.

4. Detection

There are different types of detectors, semiconductor, gas ionization detectors are some of the most frequently used [9].

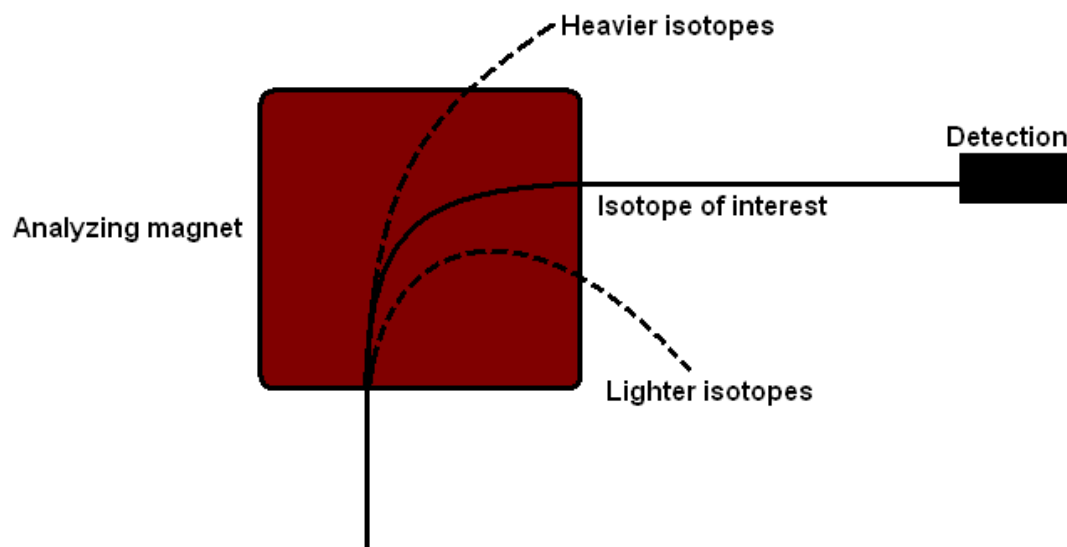


Figure 2- Sketch of a typical analyzing magnet. The ions will move in the magnetic field according to the Lorentz force [8].  $\vec{F} = q\vec{v} \times \vec{B}$  The isotope of interest follows the curved line while the dotted lines represent isotopes with too much or too little momentum that bends of and does not reach the detector.

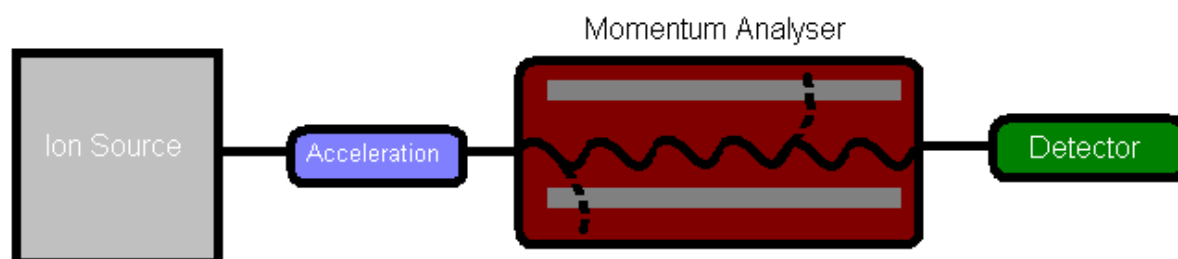


Figure 3 - Sketch of a MS system with a quadrupole momentum analyser.

Often when performing measurements, it is most simple to measure the ratio of the isotope of interest and a reference isotope, which is most cases some isotope that there is some abundance of in the sample. [9] The sensitivity is the smallest ratio that you can have between the isotope of interest and a reference isotope. Another way of determine how small quantities a method can detect is looking at the limit of detection (LOD). The LOD is the smallest amount that you can detect within a reasonable uncertainty, [14] often defined as three standard deviations from the blank value, the blank value is where we have absence of the isotope of interest. [15] The LOD is a number which defines how sensitive a measurement technique is for a specific isotope. To quantify the isotope, the limit of quantification (LOQ) is needed to be achieved, the  $LOQ \geq LOD$ . [16]

When measuring plutonium in for example bioassay, the interest could be in finding traces of the



element rather than quantifying the number of atoms in the sample. Then the amount needed of the isotope in the sample is in the LOD. In nuclear fuel, the interest is in quantifying the amount of the isotope, the lowest sample needed then is the LOQ.

Even if there are analyzing methods to separate the unwanted ions, this method is still not perfect. MS systems cannot sort out molecules with the same mass as the ion that is interesting to measure.  $^{238}\text{U}^1\text{H}^-$  could disturb the measurements of  $^{239}\text{Pu}^-$  for example. This kind of isobaric molecules can be detected and thereby disturb the sensitivity, if the mass resolution of the detector is not large enough. The same applies for ions that have the same mass/energy to charge ratio and ions which charge, mass or energy somehow have changed in the system [9]. The sensitivity of an MS can range from about  $10^{-6}$  to  $10^{-11}$ , which means that you can detect 1 isotope of interest among  $10^6$  to  $10^{11}$  reference isotopes.

Problems such as interaction from isobaric molecules disappear when there is an accelerator in the system. Otherwise the AMS system is similar to the MS system, below a description of the AMS follows:

1. An ion source

An example of ion source in an AMS system is the Cs-sputter ion source. [17] [18] Tandem accelerators which is a common accelerator type in AMS systems need a negative ion source [9], the reason is explained in the part about the accelerator.

2. Pre-acceleration

The ions are accelerated in a electric field in the kV magnitude [12]

3. Momentum Analysis

For example an analyzing magnet and/or an electrostatic analyzer can be used [18] [19]

4. Acceleration

The next step in the AMS system is the accelerator, the usually tandem accelerator with a potential of 2 to 15 MeV. [9] Because the accelerator give high energies the energy resolution is improved. [12] A tandem accelerator is like a large tank with a high voltage terminal inside that generates a positive charge. When a negative ion of usually charge -1 [12] enters through the acceleration tube, it is accelerated. In the middle of the accelerator a thin film or a gas is used to strip of electrons. [9] The stripping results in that the previous negative ion is now positively charged, for example charge 5+ or 6+. [20] If this ion is an isobaric molecule, it will decompose, and will not be detected. [9] Now the ions have multiple charges and, depending on the isotope, a specific charge/mass ratio is chosen to be analyzed. [12]

5. Abundance isotope detection

After the accelerator the reference isotope can in some cases be measured as current in a faraday cup, this current is then compared with the amount of detected ions of the isotope of interest. Sometimes the abundance of reference isotope is too low to be measured in a Faraday cup, then it has to be ion counted in the detector at the end of the system along

with the isotope of interest.

6. Momentum/Energy/Velocity analysis

There is usually at least two or more analysis steps to reject unwanted ions. These analysis can be of the same design as in point 3 for the MS [9]

7. Detection

After a number of analysis steps, depending on the system (point 6 in the description of AMS) the detection part comes, which can be done with some of the detectors mentioned in point 4 of the MS system for example.

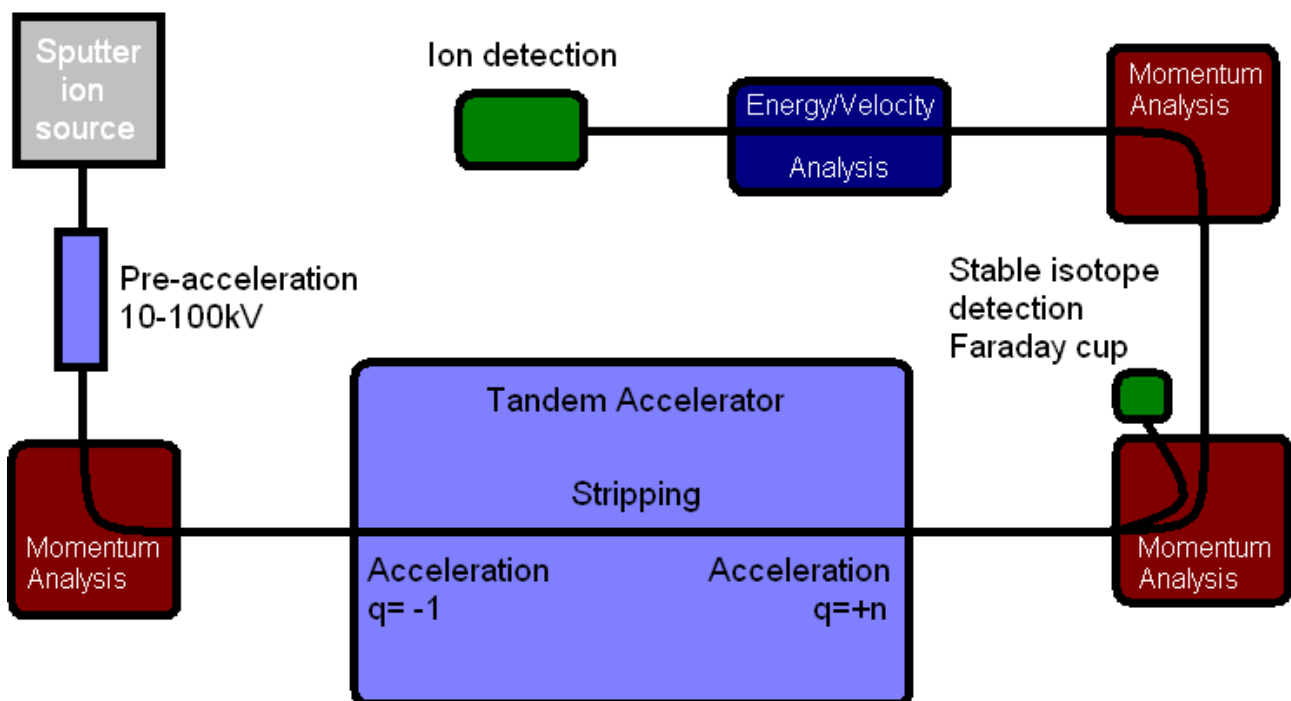


Figure 4- Sketch of an AMS system with a tandem accelerator

At present there are several applications for AMS, for example measurements in extraterrestrial materials, environmental science applications, geosciences applications such as production of radionuclide in rocks, archaeology, physics and material science, and life sciences [9]. A widely known application is radiocarbon dating which is used to measure ratio of  $^{14}\text{C}$ ,  $^{13}\text{C}$  and  $^{12}\text{C}$  in a sample to determine how old it is. This is done by measuring the ratios of these isotopes, followed by comparison with so called standards that contain a known ratio of the different isotopes.  $^{14}\text{C}$  is a radioactive isotope that decays with a half-life of 5730 years. When an organism dies it stops to renew  $^{14}\text{C}$  in it, which makes the  $^{14}\text{C}/^{12}\text{C}$  smaller for sample with an organism that have been deceased for a while, than for the standard sample for example. The amount  $\text{C}^{13}$  and  $^{12}\text{C}$  is often in enough large magnitude to be measured in a faraday cup, while the  $^{14}\text{C}$  amount has to be counted in a detector. After the isotope ratio in the sample has been measured, it can be compared with the standard and determination of the age of the sample can be made.

## 5. Studies on actinides with AMS

Measurements on some of the actinides have been done with AMS. During the last decade, some reports were published in the topic. The idea with those reports are often not to measure the content of actinides in nuclear fuel, but the content of pollution of radionuclides in bioassay from nuclear weapons, dumping of radioactive materials and also from enrichment and reprocessing plants. Therefore, various plutonium and uranium isotopes have been investigated.

The study of actinides with AMS has some differences compared to other groups of elements. This is because the actinides have no natural stable isotope to be used as reference when doing measurements. Therefore it is common to add a “spike” to the sample. A spike is a known amount of an isotope that can be used as a reference. It is therefore best to use an isotope with a long half-life. For measurements on plutonium,  $^{242}\text{Pu}$  has been used in some cases [18] [19]. When doing measurements on uranium it is not always necessary to add a spike due to the large abundance of  $^{238}\text{U}$ . Since the amount of actinides in bioassay is often very small, usually the pictogram level and a typical ion source needs a sample of the typical size 1-10mg, the extra volume is filled up by some other metal. Iron oxide has been used in some cases [18] [19].

To calculate the amount of the isotope of interest that is needed in a sample, the LOD, LOQ or the sensitivity for it is needed. But as stated previously the LOQ is equal or larger than the LOD, and it has been shown in the AMS case that these levels could in fact be the same. In a report [19] published by the Centre of AMS (CAMS) at the Lawrence Livermore National Laboratory in California, the blanks were consistently below the LOQ which was  $10^6$  atoms. From reports [19] [21] it has been expected and shown for some cases that detection limit in AMS for actinides is about  $10^6$  atoms. This could give a picture of the amount of needed sample from the spent fuel. In the future development of AMS it is possible that the technique has been refined to even better levels, one report [21] indicates that a detection limit of  $10^5$  atoms is possible.

## 6. AMS as a possible measuring technique for spent nuclear fuel

The limit LOD for the actinides and for the LOQ (for at least Pu and U) [19] is near the value of  $10^6$  atoms. If this expected value is combined with the amount of isotopes from table A1, it is possible to qualitatively calculate a lower limit for the amount of spent fuel that is needed to make a sample measurements with an AMS system:

$$m_{\text{Limit}} = \frac{n_{\text{Limit}}}{N_a} \cdot M \quad (6.1)$$

Here,  $m_{\text{Limit}}$  is the mass of  $n_{\text{Limit}}$  atoms (which is  $10^6$ ),  $N_a$  is Avogadro's number and  $M$  is the molar mass. The value of  $m_{\text{Limit}}$  is approximately  $4\text{E-}16\text{g}$  for the actinides. To calculate the sample size needed from the nuclear fuel, equation (6.2) is used:

$$m_{\text{needed}} = \frac{m_{\text{Limit}}}{p} \quad (6.2)$$

Here,  $m_{\text{needed}}$  is mass of the sample that is needed and  $p$  is the fraction of the isotope in the sample.

Calculations for the isotopes in table A1 can be found in table A5 of the appendix. From the table it is possible to see that the amount of fuel needed for measurements varies from about a tenth of a femtogram to a tenth of a nanogram depending the isotope. In table A5 it is noticeable that there are no values for  $^{238}\text{Np}$  and  $^{238}\text{Pu}$ . This is because it is not possible to make correct measurements on these isotopes due to the large interference from  $^{238}\text{U}$ . [22]

## 7. Present measuring of nuclear fuel techniques

Previously when determinating the nuclear inventory, complicated separations in combination with radiochemical analyses were used. One of the most common measuring techniques for spent nuclear fuel today is a kind of Inductively Couple Plasma Mass Spectrometry (ICP-MS), which is a mass spectrometry method [2]. Even if ICP-MS is a very sensitive method, half a fuel pellet (~2,76g) is used for measurements on the entire nuclear inventory (not just the actinides) [2].

With ICP-MS are there two possible ways determining the inventory in spent nuclear fuel, one-point calibrations and Isotope Dilution Analysis (IDA). The one-point calibration is a technique where the sample is measured and then compared with a standard. This method has its limitations because it can only be used when there are no isobaric overlaps, which means that there are only a few isotopes that can be analyzed this way. In other cases, the IDA is used to determine the inventory.

In the IDA, a spike is needed so that ratios between the added isotope and the isotope of interest by the ICP-MS. The isotope of interest can be determined by the following formula:

$$N_b^S = N_a^{Sp} \cdot \frac{1 - \frac{R_M}{R_{Sp}}}{R_M - R_S} \quad (7.1) [2]$$

$N_b^S$  is the number of the isotope of interest in the sample,  $N_a^{Sp}$  is the number of the spike isotope in the spike,  $R_M$  is the isotope ratio in the mixture of the spike and the sample,  $R_{Sp}$  is the ratio in the spike and  $R_S$  is the ratio in the sample. These ratios have been clarified in the equations below:

$$R_M = \frac{N_a^{Sp} + N_a^S}{N_b^{Sp} + N_b^S} \quad (7.2) [2] \quad \text{The ratio of isotopes in the mixture}$$

$N_a^{Sp}$  and  $N_b^S$  are the same as in (7.1),  $N_b^{Sp}$  is the amount of the isotope of interest in the spike and  $N_a^S$  is the amount of reference isotope in the sample.

$$R_{Sp} = \frac{N_a^{Sp}}{N_b^{Sp}} \quad (7.3) [2] \quad \text{The ratio of isotopes in the spike}$$

$$R_s = \frac{N_a^s}{N_b^s} \quad (7.4) [2] \quad \text{The ratio of isotopes in the sample}$$

There are a lot of different ICP-MS methods. In table A6 of the appendix, there is a list of different ICP-MS methods and what their top performances have been on different kind of sample materials.

### **8. Comparison of AMS and present measuring techniques**

To compare the different measuring techniques in this report, the value of the LOD and the LOQ has been mentioned to evaluate the performance.

Comparison between tables A6 and A5 can be made for the different detection limits. It can be found that AMS has a lower detection limit for the isotopes that is possible to compare. For most of them the difference is one magnitude or more compared to ICP-MS. When looking at the possible detection limit AMS is still better for most of the Isotopes. For the Pu isotopes that have been measured with both techniques result are yet quite similar for  $^{240}\text{Pu}$ , but for  $^{239}\text{Pu}$  the detection limit with AMS is about one magnitude better then the best results for ICP-MS and about five magnitudes better for some of the ICP-MS techniques.

In literature about AMS, [9] it is described that in the general case, AMS systems may have an abundance ratio that can be as low as  $10^{-15}$ . This is four magnitudes better than for MS systems which have a sensitivity of about  $10^{-11}$ , [9] this seems reasonable, when looking at some cases from the comparison. What should be said then is that ICP-MS is a very sensitive MS technique, it has developed a lot and is in some cases comparable with the AMS technique.

### **9. Results**

Tables A5 and A6 yield that AMS is magnitudes more sensitive than ICP-MS, which is the present measurement technique for inventory measurements on spent nuclear fuel. Depending on which isotope amount that is of interest to determine, the amount of fuel needed to make a sample to run in an AMS is expected to be in the range of a tenth femtogram to a tenth nanogram, but it is possible that the range can be as low as one femtogram to the tenth of a pictogram magnitude to achieve at least the lower limit of detection.

All isotopes cannot be measured with MS or AMS. The isobaric isotopes with the mass number 238 cannot be measured due to the large abundance of  $^{238}\text{U}$ .

### **10. Conclusions**

AMS is a sensitive measurement technique and it is more sensitive than the present technique for measuring inventory on spent fuel used by SKB. One of the reasons for that is because AMS is not affected by the interference from isobaric molecule ions. Another advantage with AMS is that the energy resolution is much better than for the MS technique, which makes it easier to disassociate energies from different isotopes. This is important because the small energy differences involved with detection, due to the small mass differences of the actinides. The problem with AMS is of

course that it is a more complicated and more expensive [15] technique than ICP-MS. ICP-MS is also a well-tried technique in the area, and is still developing. The problems with distinguishing the energy differences and isobaric molecules can never be solved with a MS-system which makes it less sensitive. Both ICP-MS and AMS are measuring techniques which can perform low-level measurements. This is not done today for inventory measurements but should in principle be possible with both of these methods. Even if there are a lot of isotopes to measure when determining the inventory, half a fuel pellet is a lot of sample material. This could be compared with the amount needed to make measurements with AMS, where quantification of an actinide isotope is possible to do in the range of femtogram to nanogram level.

With low-level measurements it could be possible to take samples from different geographies in the reactor. It could also be possible to measure the difference of isotope inventory on different locations in the fuel pellets.

According to the result, the recommendation from this report is to continue to investigate if AMS is a possible low limit measurement technique for spent nuclear fuel. The questions that this report leaves are whether it is possible to get the small sample amount needed from the nuclear fuel. And this report has not investigated the economical aspect of the subject or if it can compete with the efficiency (the time to measure a sample relative to the quality of the measurements) of the ICP-MS system.

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**12. Appendix***Table A1-Composition of actinides BWR fuel [5]*

Isotope	Amount (Fresh) (g)	Amount after 55MWd/kg (g)
U234	2.60E+02	1.05E+02
U235	3.35E+04	1.81E+03
U236	0.00E+00	4.44E+03
U237	0.00E+00	9.94E+00
U238	9.66E+05	9.27E+05
U239	0.00E+00	4.82E+02
Np238	0.00E+00	2.19E+00
Np239	0.00E+00	7.04E+01
Pu238	0.00E+00	4.23E+02
Pu239	0.00E+00	4.08E+03
Pu240	0.00E+00	1.41E+03
Pu241	0.00E+00	1.54E+03
Pu242	0.00E+00	1.30E+03
Am241	0.00E+00	5.75E+01
Am242m	0.00E+00	1.64E+00
Am243	0.00E+00	4.96E+02
Cm242	0.00E+00	3.00E+01
Cm243	0.00E+00	1.32E+00
Cm244	0.00E+00	2.52E+02
Cm245	0.00E+00	1.08E+01
Cm246	0.00E+00	3.56E+00

*Table A2-Composition of actinides PWR fuel [5]*

Isotope	Amount (Fresh) (g)	Amount after 60MWd/kg (g)
U234	2.60E+02	9.64E+01
U235	3.26E+04	2.28E+03
U236	0.00E+00	4.39E+03
U237	0.00E+00	1.50E+01
U238	9.67E+05	9.18E+05
U239	0.00E+00	7.83E-01
Np237	0.00E+00	8.67E+02
Np238	0.00E+00	3.38E+00
Np239	0.00E+00	1.13E+02
Pu238	0.00E+00	5.01E+02
Pu239	0.00E+00	5.55E+03
Pu240	0.00E+00	2.00E+03
Pu241	0.00E+00	2.12E+03
Pu242	0.00E+00	1.41E+03
Pu243	0.00E+00	5.65E-01
Am241	0.00E+00	6.02E+01
Am242m	0.00E+00	1.85E+00
Am243	0.00E+00	5.87E+02
Am244	0.00E+00	6.26E-01
Cm242	0.00E+00	3.67E+01
Cm243	0.00E+00	1.73E+00
Cm244	0.00E+00	3.23E+02
Cm245	0.00E+00	1.75E+01
Cm246	0.00E+00	5.05E+00
Cm247	0.00E+00	1.41E-01

Table A3- Isotopes that have relative high probability to SF [3]

Isotope	Half-life (in years)	SF rate (SF/decay)
<sup>234</sup> U	2,46E+05	1,64E-09
<sup>235</sup> U	7,04E+08	7,0E-09
<sup>236</sup> U	2,34E+07	9,4E-08
<sup>238</sup> U	4,47E+09	5,5E-05
<sup>238</sup> Pu	8,77E+01	1,9E-07
<sup>239</sup> Pu	2,41E+04	3,1E-10
<sup>240</sup> Pu	6,56E+03	5,7E-06
<sup>241</sup> Pu	1,43E+01	2,4E-14
<sup>242</sup> Pu	3,73E+05	5,5E-04
<sup>241</sup> Am	4,32E+02	3,6E-10
<sup>243</sup> Am	7,37E+03	3,7E-09
<sup>242</sup> Cm	1,62E+02	6,2E-06
<sup>243</sup> Cm	9,97E+01	5,3E-09
<sup>244</sup> Cm	1,81E+01	1,4E-04
<sup>245</sup> Cm	8,50 E+03	6,1E-07
<sup>246</sup> Cm	4,76 E+03	2,6E-02

TableA 4-Spontaneous fission activity

Isotope	SF rate (SF/Bq)	Concentration (g)	Activity (Bq)	SF activity (SF/s)
<sup>234</sup> U	1,64E-09	1.05E+02	7.61E+17	1.25E+09
<sup>235</sup> U	7,0E-09	1.81E+03	4.57E+15	3.20E+07
<sup>236</sup> U	9,4E-08	4.94E+03	3.73E+17	3.51E+10
<sup>238</sup> U	5,5E-05	9.27E+05	3.64E+17	2.00E+13
<sup>238</sup> Pu	1,9E-07	4.23E+02	8.46E+21	1.61E+15
<sup>239</sup> Pu	3,1E-10	4.08E+03	2.96E+20	9.17E+10
<sup>240</sup> Pu	5,7E-06	1.41E+03	3.74E+20	2.13E+15
<sup>241</sup> Pu	2,4E-14	1.54E+03	1.87E+23	4.48E+09
<sup>242</sup> Pu	5,5E-04	1.30E+03	6.01E+18	3.31E+15
<sup>241</sup> Am	3,6E-10	5.75E+01	2.31E+20	8.30E+10
<sup>243</sup> Am	3,7E-09	4.96E+02	1.16E+20	4.28E+11
<sup>242</sup> Cm	6,2E-06	3.00E+01	3.19E+20	1.98E+15
<sup>243</sup> Cm	5,3E-09	1.32E+00	2.27E+18	1.21E+10
<sup>244</sup> Cm	1,4E-04	2.52E+02	2.38E+22	3.33E+18
<sup>245</sup> Cm	6,1E-07	1.08E+01	2.16E+18	1.32E+12
<sup>246</sup> Cm	2,6E-02	3.56E+00	1.27E+18	3.30E+16

*Table A5 - qualitatively amount of spent nuclear needed to do measurements with AMS, where the expected amount of sample from fuel is calculated from the expected detection limit which is  $1\text{E}+06$  atoms. The ultimate amount of sample from fuel is calculated from the possible detection limit which is  $1\text{E}+05$  atoms.*

Isotope	Amount (g)	part of mass (%)	Expected detection limit ( $10^{-16}\text{g}$ )	Expected amount of sample from fuel (g)	Possible detection limit ( $10^{-17}\text{g}$ )	Possible amount of sample from fuel (g)
<b>U234</b>	1.05E+02	1.11E-02	~4	3.49E-12	~4	3.49E-13
<b>U235</b>	1.81E+03	1.92E-01	~4	2.03E-13	~4	2.03E-14
<b>U236</b>	4.44E+03	4.71E-01	~4	8.33E-14	~4	8.33E-15
<b>U237</b>	9.94E+00	1.05E-03	~4	3.74E-11	~4	3.74E-12
<b>U238</b>	9.27E+05	9.82E+01	~4	4.02E-16	~4	4.02E-17
<b>U239</b>	4.82E+02	5.11E-02	~4	7.77E-13	~4	7.77E-14
<b>Np238</b>	2.19E+00	2.32E-04				
<b>Np239</b>	7.04E+01	7.46E-02	~4	5.32E-12	~4	5.32E-13
<b>Pu238</b>	4.23E+02	4.48E-02				
<b>Pu239</b>	4.08E+03	4.32E-01	~4	9.18E-14	~4	9.18E-15
<b>Pu240</b>	1.41E+03	1.49E-01	~4	2.67E-13	~4	2.67E-14
<b>Pu241</b>	1.54E+03	1.63E-01	~4	2.45E-13	~4	2.45E-14
<b>Pu242</b>	1.30E+03	1.38E-01	~4	2.92E-13	~4	2.92E-14
<b>Am241</b>	5.75E+01	6.09E-03	~4	6.57E-12	~4	6.57E-13
<b>Am242m</b>	1.64E+00	1.74E-04	~4	2.31E-10	~4	2.31E-11
<b>Am243</b>	4.96E+02	5.26E-02	~4	7.68E-13	~4	7.68E-14
<b>Cm242</b>	3.00E+01	3.18E-03	~4	1.26E-11	~4	1.26E-12
<b>Cm243</b>	1.32E+00	1.40E-04	~4	2.88E-10	~4	2.88E-11
<b>Cm244</b>	2.52E+02	2.67E-02	~4	1.52E-12	~4	1.52E-13
<b>Cm245</b>	1.08E+01	1.14E-03	~4	3.55E-11	~4	3.55E-12
<b>Cm246</b>	3.56E+00	3.77E-04	~4	1.08E-10	~4	1.08E-11

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*Table A6 – LOD for various isotopes with ICP-MS methods[21]*

Isotope	Sample	Technique	Limit of detection (LOD) ( $10^6$ atoms)
$^{232}\text{Th}$	urine	PN-ICPMS-Q	3000
$^{237}\text{Np}$	Inst. Blanks	ICPMS-Q	3
$^{237}\text{Np}$	U fuel pellets	IC-ICPMS-Q	3000
$^{237}\text{Np}$	Artificial urine	ICP-MS	30
$^{238}\text{U}$	High purity water	ICPMS-DF	6
$^{238}\text{U}$	Leaves	PN-ICPMS-Q	4000
$^{238}\text{U}$	Urine	ICPMS-Q	3000
$^{238}\text{U}$	High purity water	USN-ICPMS-DF	60
$^{238}\text{U}$	Rocks	ETV-ICPMS-Q	10
$^{238}\text{U}$	Water	ETV-ICPMS-Q	7
$^{239}\text{Pu}$	Instrument limit	ETV-ICPMS-Q	2,5 (Single ion mode) 40 (Mass scan mode)
$^{239}\text{Pu}$	U fuel pellets	IC-ICPMS-Q	10000
$^{239}\text{Pu}$	Soil, pine needles	PN-ICPMS-Q	100
$^{239}\text{Pu}$	Soils	USN-ICPMS-Q	60
$^{239}\text{Pu}$	Soils	USN-ICPMS-Q	20
$^{239}\text{Pu}$	Instrument blanks	USN-ICPMS-DF	10
$^{239}\text{Pu}$	Soils	ICPMS-Q	7
$^{240}\text{Pu}$	Instrument blanks	USN-ICPMS-DF	1