様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科研費
KAKENHI

科学研究費助成事業　　研究成果報告書

平成 ３０ 年　 ６ 月 ２０ 日現在

機関番号：１２６０１
研究種目：若手研究(B)
研究期間：2015～2017
課題番号：１５Ｋ１７６３８

研究課題名（和文）Precise real-time measuring gadolinium concentration in water

研究課題名（英文）Precise real-time measuring gadolinium concentration in water

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交付決定額（研究期間全体）：（直接経費）　　2,300,000円

研究成果の概要（和文）：AASを用いたGd濃度測定：我々は、Ta及びWを用いた測定を開始し、2016年には、Ta及びW両方で高精度のGdの濃度測定に成功した。使用していたセルの製造元の日立製作所が製造を中止した為、論文が中断している。我々は新しいセルにあわせてデザインを行っており、最終結果を論文にまとめる予定である。
Gdの磁気モーメントを用いた測定：我々はいくつかの測定器のデザインで実験を行ったが、期待される感度に到達出来なかった。その原因として、十分な性能を持った装置を制作する為の予算不足が挙げられる。実験提案書中でも示したように、原理的には測定は可能であるので、今後も実現を目指して試行を進めていく予定である。

研究成果の概要（英文）：Gd concentration with AAS: In 2015 tests started using tantalum (Ta) and Wolfram (W) plates. By 2016 very good results were achieved with both Ta and W. Each material has its advantages and its drawbacks: Ta is very easy to work with but it is less resistant to high temperatures. W is more difficult to shape and fit in the AAS' cuvettes but it is much more resistant to high temperatures. In 2017 we were planning to publish a paper but Hitachi stopped the production of its cuvettes. We are now adjusting our design to the new ones before publishing resulting in a temporary delay.
Using Gd magnetic properties: We did several device designs but we didn't reach the required sensitivity. We may have done a mistake in evaluating the feasibility of this technique with such a cheap cost. As demonstrated in our proposal the principle is correct and feasible but given our budget constraints to build this device, it may not be possible. Nevertheless, we are still trying and did not give up yet.

研究分野：astrophysics, high energy physics

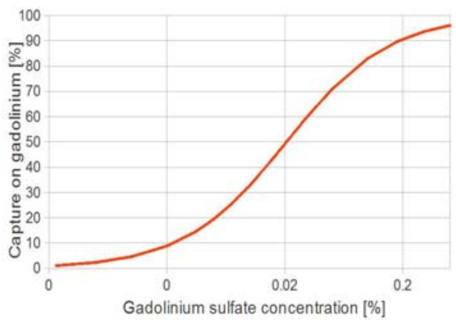
キーワード：gadolinium　concentration　measurement

１．研究開始当初の背景

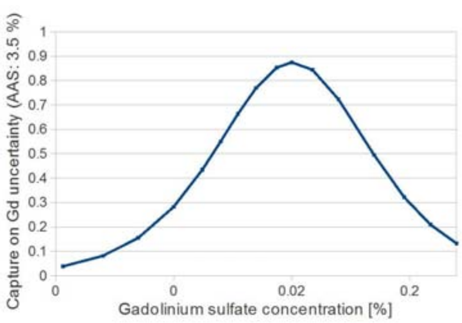
Ultra-pure water Cherenkov detectors cannot detect neutrons efficiently. In pure water, neutrons are usually captured on protons and produce a single 2.2 MeV gamma which can be detected with low efficiency only. Enabling neutron detection would allow us to distinguish inverse beta decays from other events and thus, reduce backgrounds in many current analyses at Super-Kamiokande (SK).
Following the GADZOOKS! proposal[1] we plan to dope SK with 0.2% in mass of gadolinium (Gd) sulfate. This has even been proposed for future detectors like Hyper-Kamiokande[2]. Neutron capture on Gd produces a gamma cascade of about 8 MeV total energy, which can be detected with high efficiency.

２．研究の目的

Our purpose is the measurement of the Gd concentration in water. The reason is that we need to know the probability of neutron captures on Gd and on protons. The uncertainty of neutron captures on Gd depends on its concentration. The figure below shows the captures [%] on Gd as a function of the Gd sulfate concentration:



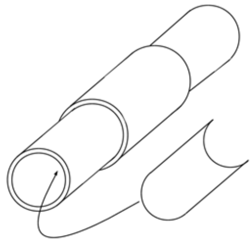
If we measure Gd concentration with a 3.5% uncertainty, the neutron capture uncertainty in Gd as a function of the Gd sulfate concentration is shown below:



At the target concentration of 0.2% Gd sulfate we have a 0.3% uncertainty with a maximum at a concentration around 0.02% of 0.9%.
Other applications are: monitoring of Gd losses in our water purification systems, measure the homogeneity of the concentrations in our detector or, in case we need to remove Gd, confirm its removal from water before disposal.
Our goal is to further improve the methods we developed in the past to measure these concentrations.

３．研究の方法

We proposed two methods:
The first method consists in improving the current method. We developed a method to measure Gd using an atomic absorption spectrometer (AAS). Our improvement targets the main drawbacks of the current method. It consists on adding a foil of tantalum (Ta) or Tungsten (W) inside the AAS' cuvette.

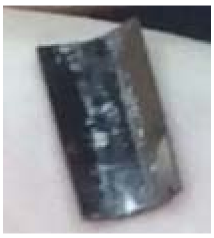
The cuvette is shown on the left picture above. Its schematic representation is shown on the right together with a possible foil shape to be inserted.

The second proposed method is to use the magnetic properties of Gd to perform concentration measurements. Gd is ferromagnetic below 17ºC and strongly paramagnetic at higher temperatures.
If we apply a known magnetic field to a sample and measure the resultant magnetic field we can measure the magnetic susceptibility which depends on the Gd concentration.
The advantage of this method (and main motivation to pursue it) is the possibility of continuous monitoring of the Gd concentration in our detector. In principle, the susceptibility may change in presence of iron, nickel or cobalt but these elements are not diluted in our detector. Only iron in case of rust in the stainless steel structure could modify this but this would be seen in the water transparency (ppb levels of iron drastically reduce water transparency to Cherenkov light).

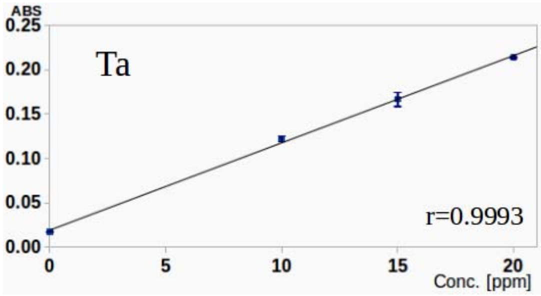
４．研究成果

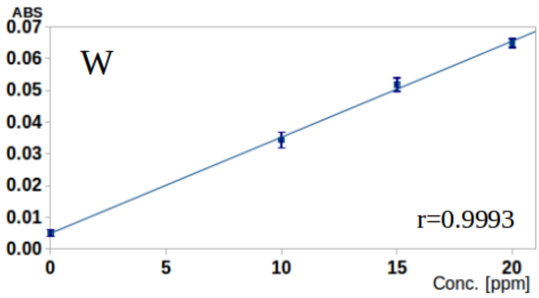
After purchasing Ta and W foils we realized the difficulty to machine them ourselves. We found a company in our region that was able to cut these materials with the precision and care needed for our purposes. The technique they use was the electrical discharge machining. It performs clean and precise cuts in Ta and W.
Standard cuvettes have a structure similar to two concentric cylinders with a middle section of larger diameter than the two outer sections (see figures above). There are cuvettes that in addition have a platform inside.
We tried with platform cuvettes: on top of the platform we added a Ta or a W foil of similar size and same shape. The results were not as desired because these cuvettes work at atomization temperatures of maximum 2800°C. While Ta and W allow for better atomizations, the lower temperatures yield to weaker signals.
With tried with standard cuvettes and several foil designs too. The most successful ones have been Ta and W foils that are inserted in the middle section of the cuvette.
We fabricated moulds for foils of different radii to form the Ta and W foils (to test mechanical stability inside the cuvette during atomization). At this stage we realised that W is more difficult to work with than Ta. W is brittle at room temperature. Forming W has to be done at about 300°C. To heat W we have tried using a solder iron and a heat gun. In both cases we achieve the desired results but they are somewhat primitive and cumbersome techniques that we want to improve.
The figure below shows formed Ta:

The figures below show W without (left, broken or with a kink) and with pre-heating (right, round shape):



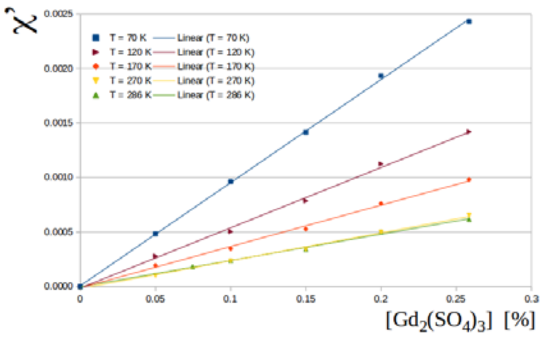
After trying several sizes and shapes we found an optimal design.
We studied the linearity, stability and lifetime of the cuvette-Ta/W foil tandems. Below and example for both Ta and W:





In the figures above we see good linearity for concentrations between 10-20 ppm Gd sulfate. About 10 dummy Gd measurements were needed to condition and stabilise the cuvette-foil tandems. Different temperature programs were used to optimize the signal but the results are similar.
Foil lifetimes are about 80 atomizations for Ta and about 100 for W. Ta has a longer lifetime, probably due to its higher melting point (Ta: 3017°C while W: 3422°C). However, since Ta is easier when forming the foils this looks like the preferred material to use.
The measurements time are reduced by 75% and makes them simpler.
We were planning to publish these results but Hitachi, the cuvette maker, discontinued the production of cuvettes. Now we are adjusting our design (basically radius of the foil) before going for publication.

While Gd is ferromagnetic below 17°C and strongly ferromagnetic above this temperature, we had to prove the magnetic susceptibility varies linearly with a Gd sulfate solution. The figure below shows the magnetic susceptibility of Gd sulphate solutions in the range of 0.05-0.26% in mass concentrations and for several temperatures from 70K to 286K. These data was taken with a SQUID (from the



ISSP of the Univ. of Tokyo in Kashiwa). The magnetic susceptibility has been corrected here to account for the pure water and sample container. Variations from the Gd sulphate are shown only and a very good linearity is observed. This is a proof of principle of the proposed technique.
The next step was to try with helical resonators (working as a filter resonator). The idea is that when having water of different Gd concentration in the resonator and using a vector network analyser, the filtered frequency will change too. The change thus, would allow us to measure the Gd concentration. Below an example of one of the tested before being fully mounted:

The frequency and quality factor of the device depends on several factors like helix diameter and height, and number of turns of winding[1].
After several designs and trials we have not reach the desired sensitivity. Even though we have demonstrated the proof of principle, at this point, we wonder whether we were too optimistic when evaluating the feasibility with such a low cost.
Nevertheless, we are still trying several improvements and did not give up yet completely the idea.

List of References:

[1] J. F. Beacom and M. R. Vagins: GADZOOKS! Anti-neutrino spectroscopy with large water Cherenkov detectors. Phys.Rev.Lett. 93 (2004) 171101.
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[4] W. W. Macalpine, R. O. Schildknecht: Coaxial Resonators with Helical Inner Conductor. Proc. of the IRE 47(12) 2099-2105.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔学会発表〕（計　2　件）

Super-Kamiokande Gadolinium R&D Project: Methods to measure Gd concentration in ultra-pure water. JPS Autumn meeting, 2016. By <u>Lluis Marti-Magro.</u>
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