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To whom it may concern.

Report on the dissertation submitted by Chavdar Dutsov, to the department of Atomic Physics of the Sofia University "St Kliment Ohridski" for the fulfilment of the requirements for the degree of Doctor of Philosophy.

Studies on the applications of the Triple-to-Double coincidence ratio method for primary standardization of activity using liquid scintillation counting.

The document is structured in three main parts and divided in eleven chapters.

The first part is devoted to the description of liquid scintillation counting (LSC) and its applications for radionuclide metrology. This part is the result of an extensive bibliographical study of the subject, from the origin of the LSC in the mid XX century, to the latest developments. The description of the molecule's excitation phenomena from the ionizing radiation is of high importance, as the mechanisms described illustrate the timing properties of the liquid scintillator, which are used in this work. Details are given on the dependence between the absorbed energy and the number of photons produced, and the non-linear phenomena involved. Some details are also given on the detectors used in LSC, the photomultiplier tubes (PMT), as their dynamic properties influences the methods to be used for data processing. Then, the main method used in LSC for metrological applications, the free parameter model, is described in details, with an exhaustive description of the coincidence equations. All this part, strongly documented, gives the basis for the study developed in this document. Some common applications of this free parameter model, like the Triple to Double Coincidence Ratio method (TDCR) are described, together with more exotic approaches like the Compton coincidence related methods. I consider that this first part gives all the useful information needed to understand the study and developed in the following parts of the document.

The second part is devoted to the description of timing aspects in the light emission, and how this information could be used in radionuclide metrology. C. Dutsov developed a computation program to analyse and classify the detected light pulses events, with considerations on the necessity to add dead-time in the data processing, in order to reject spurious events. This program was also validated by a Monte Carlo simulation module, also developed by the author. This analysis allowed the comparison of possible coincidence counting algorithms, validated by experimental results. Some considerations are given on the prompt and delayed light emission of the scintillator, which are the cause of considerable problems in metrology using LSC. Developments are given on the establishment of the cross-correlation function describing the time domain relationship between the signals given by the PMTs. The relation between the characteristics of this cross-correlation function, and the number of photons emitted, is derived, giving the possibility to develop a new way to deduce the detection efficiency of a radionuclide from this cross-correlation function. It must be stressed that this method is a very original approach which was never used previously.

The third part described some applications of the time distribution approach in radionuclide metrology. The first one, is related to the measurement of the half-life of some excited nuclear states following the radioactive disintegration. Practical examples are given for ^{57}Fe and ^{237}Np, leading to the measurement of precise new values which will be of practical interest for the improvement of nuclear databases, widely used in the international radionuclide metrology community. It must be pointed out that, in some cases, Chavdar Dutsov used an original approach to analyse these half-lives from a liquid scintillation counter.

The second application concerns the establishment of a method to evaluate and correct the accidental coincidences in TDCR counting. This point is of paramount importance in TDCR metrology, as this allows the possibility to measure radionuclides with high activity or to use extended coincidence resolving times. The calculation methods developed and tested by Chavdar Dutsov give practical tools which will be of considerable interest for the international radionuclide community using LSC.

The third application addresses the important and still open question of how to manage delayed fluorescence in LSC, with the practical problem of the optimal coincidence resolving time. The discussion is of practical interest for the radionuclide metrology community and gives useful arguments to optimize the coincidence resolving time necessary to record most of the light emission, but avoiding the drawbacks related with the detection of delayed light emission.

The fourth application described in this section is related to the development and use of a Compton coincidence LS detector, allowing a considerable improvement to the TDCR method. Chavdar Dutsov developed specific software packages to process the data of this counter produced by a list-mode approach. This approach led to a considerable improvement of the practical efficiency of Compton coincidence experiments, which are known to be very lengthy. Many experimental results are commented in this section, representing a remarkable synthesis on the possibility of the Compton coincidence method in radionuclide metrology.

The last application described in this part of the document are related to the use of the TDCR method at the Sofia University. This includes a successful participation to an international comparison exercise for the international standardization of a tritiated water solution, and a participation to two international comparisons of the activity of radon-in-water, and the measurement of radon behaviour in polymers. It is shown that the instruments and methods developed at the laboratory of ionizing radiation of Sofia University, placed this laboratory at the best international level in radionuclide measurement by LSC.

The document is well structured, and the chapters are articulated in very logical sequences. The text is easy to read and will provide very valuable information to specialists of TDCR counting in LSC. Chavdar Dutsov did a considerable work in this field, with intensive analysis of the physical and statistical phenomena involved in LSC methods. This allowed him to develop innovative software to process information delivered by TDCR counters. From this work I consider that Chavdar Dutsov is now an expert of the TDCR method in LSC and his contributions will be very useful to the radionuclide metrology international community, including the ongoing developments on international traceability under the auspice of the Bureau International des Poids et Mesures (BIPM). The evaluation method of accidental coincidences established by Chavdar Dutsov is already implemented in the new extension of the international reference system (ESIR) for pure beta and electron capture radionuclides.

In short, this dissertation is an outstanding contribution to the field of radionuclide metrology by LSC, introducing new and original developments which will give rise to innovative methods in radionuclide metrology. I consider that this dissertation completely fulfils the requirements for the degree of Doctor of Philosophy. I can also add that, during my activity of Research Director at LNHB, France, I rarely saw a thesis such high level.

Dr Philippe Cassette July 4th, 2021