STUDY AND DETERMINATION OF THE RATIO ATOMS BETWEEN HYDROGEN AND MANGANESE IN THE MANGANESE SULPHATE BATH: PROCEDURE AND CALCULATION

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ABSTRACT

The Brazilian Neutron Laboratory (LN) is part of the National Laboratory of Ionising Radiation of Metrology (LNMRI/IRD). It operates a system for absolute standardization for the measurement of the neutrons sources fluence. The Manganese Sulphate Bath (MSB) is part of this measurement system and was donated by the Bureau International de Poids et Mesures (BIPM) in 1996. Since then at LN has become a fulfilled inquiry and measurements of fluence rate of a neutrons source Q. LN has carried through activities for the maintenance and dissemination of the reference values for this primary standard. Currently LN advances in two work lines: One of them is the study of the bath sensibility of the detection system (e), and the other is the study of f parameter, that measures the fraction of captured neutrons by ⁵⁵Mn. In the present work, we dedicate special attention to the measurement of the neutron fraction that depends on the amount of ratio atoms between hydrogen and manganese. A revision of the procedures and the experience involved with the measurement system gave chance to evaluate points for a metrology refinement leading to lower uncertainties and greater reliability degree values. To obtain the cited refinement, the following stages had been fulfilled: Firstly, the development of a tool for confection of standardized crucibles. Secondly, the characterization of the muffle used in the work through the survey of heating slopes. And finally, the study of the volatility with the temperature of manganese sulphate (MnSO₄ + H₂O) through a thermo-gravimetric analysis in the own muffle conditions used in the work. It was observed that the steady temperature of operation in the quantification of the Manganese in the solution meets above of 350 °C and this caused a significant improvement over the measurement proceeding. This work demonstrates that the improvements in the proceeding for the determination of the NH/NMn ratio leads to the one of the goals longed for this Laboratory.

1. INTRODUCTION

The Neutrons Laboratory (LN) pertaining to the National Metrology Laboratory for Ionized Radiation (LNMRI/IRD) operates a system used to absolute standardization of neutron sources donated by the Bureau International de Poids et Mesures (BIPM) in 1996. In the LN there is a permanent inquiry work through this system in which the Manganese Sulphate Bath (MSB) of the static type is used as measurement method of fluence rate of a neutron source Q(t) and from influence variables in the measurement. The MSB consists of a supplied spherical cavity with 520 L of aqueous manganese sulphate solution (nMnSO₄+mH₂O). The source to be measured is put inside the solution, located in the cavity center which in consequence of nuclear reaction is activated reaching the saturation approximately after 25 hours of irradiation period. After that, the source is removed and then the solution is agitated for ten minutes period to achieve an homogeneous distribution of nucleus activated. After homogenization, a sodium iodide detector is inserted in the bath so that the decline of ⁵⁶Mn activity can be followed until thirty counting measurements with 500s each is done (variable in function of the activity). For each measurement, the counting rate is corrected for the value of the saturation activity A(t) being the average value of this activity used in calculations of
the neutron source fluence \(Q(t)\) by means of expression (1) where influence terms in measurements are considered. We can admit that the manganese does not absorb all source emitted neutrons and that others losses influence in the measurement.

\[
Q(t) = \frac{A(t)K}{\varepsilon f}
\]

(1)

- \(A(t)\) \(^{56}\text{Mn}\) saturation activity in solution.
- \(K\) Correction term
- \(\varepsilon\) Sensitivity of the detection system.
- \(f\) Thermal neutron fraction captured by \(^{55}\text{Mn}\).

The \(^{56}\text{Mn}\) saturation activity \(A(t)\) in solution is gotten directly by means of the measurement in counting electronic system with a NaI (Tl) detector which measures \(^{56}\text{Mn}\) decline produced in the bath through the nuclear reaction of thermal neutrons with stable \(^{55}\text{Mn}\) nucleus. \(K\) correction term which is related with the neutron escape, fast neutrons captured by material source and fast neutron capture in solution was determined by means of the MSB mathematical simulation in a previous work [1]. The \(\varepsilon\) term represents the efficiency of the standardization system, determined by means of the absolute standardization of the activity from a collected solution sample of the MSB irradiated with a high thermal neutrons fluence. Finally, \(f\) term depends on the atoms amount in solution and in particular from the number of atom ratio between hydrogen and manganese.

2. OBJECTIVE OF THE WORK

The objective this work is to determine the ratio \(N_{\text{H}}/N_{\text{Mn}}\) which is an important factor in the \(f\) term calculation from equation 1. The values will be used in future mathematical Monte Carlo simulations from MSB. This work has for purpose an evaluation in retrospect of the measured values and its respective uncertainties as well as of the used methods considering, in such a way, a new methodology for the calculation procedure. The spreading of a standardized methodology for the determination \(N_{\text{H}}/N_{\text{Mn}}\) ratio facilitates measurements for inter-laboratorial comparison. It is expected to obtain measurements from physical amount values to better define MSB one a way simpler than the current one, objectifying a value of more trustworthy \(f\) term and with a lesser uncertainty.

3. METHODOLOGY FOR THE MEASURE OF THE REASON BETWEEN ATOMS OF HYDROGEN AND MANGANESE

The methodology for the measurement from the ratio between atoms of hydrogen and manganese is based on gravimetrical methods carried out in the own neutron laboratory with the lesser possible uncertainty. The previous LN procedure was analyzed and was observed that the uncertainties was dependent from operators, scale resolution, mass solution sample, crucible mass, number of measurements and volatization temperature of total water with MnSO₄ solution samples. The used gravimetrical method allows the determination of the ratio atom number between H and Mn from relative concentration between H and Mn in the solution. The sample is mass determined before and after heating until total hidratation water is out. In previous works [2,3] it is recommended to heating samples until reach 300°C. There was a doubt on the temperature to use in the system of the LN. A termogravimetric analysis carried through in the LAPIN from Macro-molecule Institute Heloisa Mano of the UFRJ confirmed the temperature of 300°C to leave samples free from all hidratation water. However, being the volatization carried through in the conditions of the LN it was observed that this value is not appropriate. In accordance with the LN system of heating, the right
temperature to become the measurements of sample mass is in the interval (400-450)°C and would be superior, as observed in the graph of the mass variation with the temperature of the sample. In accordance with the termogravimetical analysis in the experimental arrangement of the LN of figure 1 the value upper 400°C is the most appropriate in this system allowing to minimize the uncertainties. From this analysis it was concluded that the temperature of 300°C was a critical temperature and of sample instability in the volatization system, therefore it still lost mass with much rapidity.

![Figure 1. Variation of the loss of mass of the solution of MnSO4 with the temperature.](image)

A tool projected and was constructed for the production of identical crucibles of Al (Figure 2).

![Figure 2. Tool for construction of identical crucibles.](image)

### 3.1. Procedure.

The procedure was conceived as a sequence of operations that had allowed evaluating the ratio $N_{H}/N_{Mn}$ with the lower possible uncertainty. This procedure characterizes itself by the applicability, uncertainty and exactness of its results. The reached degree of uncertainty was opted due to its easiness use and execution which allows working with a minimum amount of samples.
The thermo-gravimetric method is a physical method, therefore the MnSO$_4$ does not suffer modification in its composition in consequence of determination process of ratio $\frac{N_H}{N_{Mn}}$. Thermo-gravimetry (TG) is an analytical method in which the variation of mass of a substance is measured in function of the temperature while the sample is submitted to a controlled atmosphere. The micro-gravimetical term and micro analysis must be to use in this work due to order of magnitude of the amounts of the samples and in face of the sensitivity of the analytical scale that is of the order of 10-5g. The generalized extension of the gravimetrical method in the determination of a micro amount requires the development of one adequate technique. Due the above considerations under the aspect of the sample amount used in this procedure we can classify it as a micro method in accordance with the classification of KIRK [4]. In the same way, that a macro analysis, the micro analysis relatively requires cares and attention to the errors of the technique and instruments. The domain of the technique is reached by means of the experience having required a period of training of the analyst to enable it and to qualify it the practical one of the microanalysis. In the micro-gravimetical method the mass of a sample of the BSM is determined. After that the Manganese Sulphate is separate of the solution of the BSM for removal of the water for the heat. In the form of the MnSO$_4$ composition finally it is weighed and it made a difference between the masses final and initial of the sample to determine the relative concentration of H and Mn in the solution. It is determined fraction volatilized for the difference before enters the masses and after the volatization.

3.3. Crucibles.
Previously the measurements were carried through for a porcelain crucible. The use of a porcelain crucible introduced an error in the measurements due to porcelain to be hygroscopic. Later this porcelain crucible was substituted by one another one of platinum. This for having a bigger capacity many times from samples amount, also absorbed highly humidity, influencing measurements. A smaller platinum crucible was used in posterior measurements, but its mass was still very superior to the sample masses. Crucibles made from aluminum foils have been manually confectioned and the first measurements yielded to lower uncertainties. So the new measurement procedure was suggested and initiated the first inquiries and questionings on the previous procedures.

3.4. Materials.
- ANALYTICAL SCALE METTLER model H15 Nº Series: 175436; band of 0-160 g, measurement sensitivity up to 1,0 x 10$^{-4}$ g.
- MUFFLE.
- THERMOMETER SALVTERM 1200.
- PIPETTE.
- CRUCIBLES OF ALUMINUM FOILS.

4. RESULTS
The results of measurements are presented in the table 1. In table 2 one meets an evaluation of the measured values reproducibility and repeatability and its respective uncertainties for two different operators, measuring the MSB physical amounts under the same conditions.
### Table 1. Uncertainties comparison.

<table>
<thead>
<tr>
<th>Reproducibility</th>
<th>Density g/cm³</th>
<th>u %</th>
<th>u abs</th>
<th>Repeatability</th>
<th>H₂O u %</th>
<th>u abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operador 1</td>
<td>1.3813</td>
<td>0.048</td>
<td>0.0007</td>
<td>3</td>
<td>0.9383</td>
<td>0.036</td>
</tr>
<tr>
<td>Operador 2</td>
<td>1.3728</td>
<td>0.024</td>
<td>0.0004</td>
<td>3</td>
<td>0.9308</td>
<td>0.095</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reproducibility</th>
<th>MnSO₄</th>
<th>u %</th>
<th>u abs</th>
<th>Repeatability</th>
<th>NH/NMn u %</th>
<th>u abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operador 1</td>
<td>0.4430</td>
<td>0.130</td>
<td>0.0005</td>
<td>3</td>
<td>35.54</td>
<td>0.135</td>
</tr>
<tr>
<td>Operador 2</td>
<td>0.4420</td>
<td>0.130</td>
<td>0.0005</td>
<td>3</td>
<td>35.33</td>
<td>0.224</td>
</tr>
</tbody>
</table>

### 5. CONCLUSIONS

The MnSO₄+H₂O solution was characterized by TGA Instrument Q500 V6.7 Build 203, with heating rate of 1.50 °C/min in nitrogen flow, in the interval of temperature from 25°C to 700.00 °C. The thermo-gravimetrical curves of hydrated MnSO₄ gotten by empirical method and with conventional equipment of LAPIN/UFRJ have been analyzed showing that the temperature in the range of 400 to 450°C is ideal to guarantee sample dehydration for measurement of ratio NH/NMn and its uncertainty. In this way the LN can introduce some modifications in the old measurements procedure of earning bigger trustworthiness, getting lower uncertainty.

The modification proposal in the ratio NH/NMn measurement procedure between atoms of H and Mn causes a sensible reduction in the uncertainty of measurements, assuring one better metrological quality. This fact can be proven by the comparison with measured values displayed in table 1. The order of magnitude gotten in the measurements with the application of the micro-gravimetrical method justifies the use of a scale with one better resolution.

### ACKNOWLEDGMENTS

We would like to acknowledge to the IRD post-graduated coordination, LN/LNMRI and LAPIN/UFRJ laboratories.

### REFERENCES