# Analysis of commercial supplements using a nuclear and MALDI-MS techniques

Marija Janković, Filip Veljković, Nataša Sarap, Suzana Veličković, Ivana Stajčić, Marija Šljivić-Ivanović, Bojan Janković

***Abstract*—This paper presents application of a nuclear technique for the analysis of radioactivity in supplements using gas proportional counter as well as application of analytical technique Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS) in order to characterize the radioactivity contents and stability of the chemical structures for commercial supplements. Gas proportional counter enables to determination of gross alpha and gross beta activity in the environmental samples, where they are present as ultra trace elements. Also, MALDI-MS method is used, since it represents an excellent analytical technique for detecting large number of biologically important molecules, such as commercial supplements.**

***Index Terms*—gas proportional counter, alpha/beta activity, MALDI-MS, supplements.**

## I. Introduction

Applications of nuclear techniques present a particular interest for the measurement of alpha and beta radiation from different environmental samples. Alpha/beta gas proportional counter is one of the instruments that are usually used in a nuclear radiation measurement laboratory. This counter enables measurement of alpha and beta radiation individually in alpha mode, beta mode or simultaneously in alpha/beta mode. Measurements allow determination of emitters that are belonging to the natural radioactive chains or determination of artificial radionuclides such as $^{90}$Sr (pure beta emitter) in environmental samples [1,2]. The main advantages of using gas proportional counter are rapidity, low detection limits in measurement, rapid preparation of the samples in case of accidental situations. Radiological characterization of the samples is important in the aim to ensure radiological protection of the public. The disadvantage of gas proportional counter use is in the qualitative determination of individual radionuclides for which another technique is needed (gamma spectrometry, liquid scintillation spectrometry, alpha spectroscopy).

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) become one of leading analytical method for various applications that range from detection of small-bioactive to large macromolecules. High efficiency in biomolecules analysis, high speed and sensitivity of analysis and wide applicability with a good tolerance toward contaminants are some of advantages this analytical method offers [3,4].

This study aimed to determine gross alpha and gross beta activity in the most popular supplements: Mg, Zn, Pepto soda B complex, C, Ca and $D_3$, available for adults. MALDI-TOF MS analytical technique was applied in B complex to detect biologically important molecules.

Marija Janković, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Radiation and Environmental Protection Department, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia (e-mail: marijam@vin.bg.ac.rs).

Filip Veljković, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Department of Physical Chemistry, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia (e-mail: filipveljkovic@vin.bg.ac.rs).

Nataša Sarap, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Radiation and Environmental Protection Department, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia (e-mail: natasas@vin.bg.ac.rs).

Suzana Veličković, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Department of Physical Chemistry, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia (e-mail: vsuzana@vin.bg.ac.rs).

Ivana Stajčić, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Department of Physical Chemistry, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia (e-mail: ivana_r@vin.bg.ac.rs).

Marija Šljivić-Ivanović, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Radiation and Environmental Protection Department, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia (e-mail: marijasljivic@vin.bg.ac.rs).

Bojan Janković, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, University of Belgrade, Department of Physical Chemistry, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia (e-mail: bojan.jankovic@vin.bg.ac.rs).

## II. The Method

8 supplements (Mg, Zn, Pepto soda B, C, Ca, $D_3$ and Zn for children) commercially available were provided in the local pharmacies.

For the gross alpha and gross beta activity measurements, samples were powdered and homogenized. From the total mass of the prepared sample, about 130 mg was weight in Al planchet and fixed with the alcohol [5]. Meaurements were performed by the gas low-level proportional counter Thermo-Eberline FHT 770T. The counting gas is a mixture of 90 % Ar and 10 % methane. Efficiencies were determined using the certified radioactive calibration standards $^{241}$Am and $^{90}$Sr (9031−OL−334/11 and 9031−OL−335/11, respectively, Czech Metrology Institute), traceable to the BIPM. $^{241}$Am has higher alpha particle energy (5.49 MeV) than those emitted by naturally occurring U and $^{226}$Ra radionuclides. $^{90}$Sr in equilibrium with its daughter $^{90}$Y is the prescribed radionuclide for gross beta calibration.

The counting efficiency was 26 % for alpha and 35% for beta radiation. Measurement time was 14400 s. Measurement uncertainty was expressed as an expanded measurement uncertainty at the confidence level of 95% (k=2).

MALDI-MS method was applied for vitamin B complex, obtained in the form of a tablet that was squashed to powder in a pestle with mortar. The obtained powder was dissolved in

 ISBN 978-86-7466-970-9

acetonitrile and then mixed with 3 different type of matrix (DHB/9AA/PA). Sample was placed on MALDI steel well plate for drying on room temperature. Mass spectra were recorded in positive, reflectron mode on AB Sciex MALDI TOF De Voyager Pro.

## III. Main Results

The characteristics of investigated supplements are given in Table 1. The analyzed samples contained different mass of elementary vitamins.

The results for gross alpha and gross beta activity in analyzed supplements (Mg, Zn, Pepto soda B, C, Ca, $D_3$ and Zn for children) are presented in Table 2. In all analyzed samples gross alpha and gross beta activity were below the minimum detectable activity (*MDA*). For gross alpha activity, *MDA* were in the range of <0.118 Bq/g (Zn tablet) to <0.193 Bq/g ($D_3$ vitamin in tablet). The *MDA* for gross beta activity were in the range of <0.240 Bq/g (Pepto soda tablet) to <0.274 Bq/g (vitamin C in tablet). Minimum detectable activity is given with the following equation:

$$MDA = \frac{LLD}{m} \qquad (1)$$

where *LLD* is detection limit (cps), *m* is mass (g).

The gross beta activity in samples is mainly due to the presence of $^{40}K$ but also can be due to artificial radionuclides $^{137}Cs$ and $^{90}Sr$, while the gross alpha activity in the samples originates from the decay chains of $^{238}U$ and $^{232}Th$. As can be seen from Table 2, *MDA* values are different. Given in mind that *LLD* from equation (1) includes efficiency for detectors and background (empty Al planchet), the calculated *MDA* differs from position to position where the samples were measured (counting system has 6 detectors and enables simultaneous measurement of 6 samples). For solid deposits, in thick sources problem with self-absorption can be present when determining gross alpha activity [6]. Self-absorption increases with the density of the source material and with the size and charge of the emitted particle. To avoid self-absorption, the maximum calculated quantity in the planchet for gross alpha activity is 130 mg, and for gross beta is 260 mg. For further analysis, in order to qualitatively determination of the radionuclides present in the samples, it is necessary to apply the gamma spectrometric method. From the decay of radionuclide contained in the samples, the effective dose of ionizing radiation can be assessed and radiological risks can be evaluated.

In the Republic of Serbia, there are no recommended levels of radionuclides in supplements. The radionuclide content limits in solid drugs are equal to the prescribed content limits for drinking water expressed in Bq/kg where volume of 1 l of water is replaced with mass of 1 kg. Recommended values in drinking water for gross alpha and gross beta activity in drinking water are 0.1 Bq/l and 1 bq/l, respectively [7].

TABLE I
Characteristics of Supplements

| Sample | Manufacturer | Content of vitamin |
|---|---|---|
| Mg | Alkaloid | 400 mg |
| Zn | Anafarm | 7 mg |
| Pepto soda | Goodwill Pharma | Sodium bicarbonate 1940 mg |
| B complex | Galenika | B1: 3 mg; B2: 3.4 mg; B6: 2 mg; B12: 1 μg; B3: 25 mg; B5: 5 mg |
| C | Cevital Essensa | 500 mg |
| Ca | Solevita | 400 mg |
| $D_3$ | Eunova | 50 mikro |
| Zn | Inpharm | 5 mg |

TABLE 2
Gross Alpha and Gross Beta Activity in Supplements

| Sample | Gross alpha activity (Bq/g) | Gross beta activity (Bq/g) |
|---|---|---|
| Mg | < 0.140 | < 0.249 |
| Zn | < 0.118 | < 0.252 |
| Pepto soda | < 0.120 | < 0.240 |
| B complex | < 0.155 | < 0.247 |
| C | < 0.164 | < 0.274 |
| Ca | < 0.179 | < 0.272 |
| $D_3$ | < 0.193 | < 0.247 |
| Zn for child | < 0.177 | < 0.273 |

Figure 1. presents MALDI-TOF mass spectra of vitamin B. In the positive mode, the presence of vitamins B1 (thiamine), B2 (riboflavin) and B3 (niacin) was observed. The peaks observed at m/z 122 and 144 represent fragment ions of vitamin B1, while the peak at m/z 265 is the molecular ion of vitamin B1. The peak at m/z 123 represents the protonated molecular ion of vitamin B3, i.e. nicotinamide. The peak at m/z 377 is the precursor ion of vitamin B2, and the fragment ion at m/z 243 is lumichrome, which is formed by the photolysis of riboflavin during analysis.

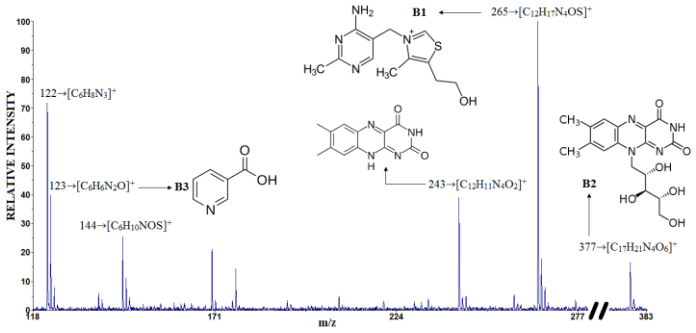


Fig. 1. Positive mode MALDI-TOF mass spectra of vitamine B

 ISBN 978-86-7466-970-9

## IV. Conclusion

In order to determine radionuclide content in supplements, nuclear technique using gas proportional counter was performed. Gross alpha and gross beta activity were determined in 8 supplements. In all analyzed samples, gross alpha and gross beta activity were below the *MDA*. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry analytical method was applied for B complex to detect molecules. Mass spectra for B complex show the presence vitamins B1, B2 and B3 in the positive mode.

## Acknowledgment

The research presented in this paper was done with financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, within the funding of scientific research work at the University of Belgrade, Vinča Institute of Nuclear Sciences (Contract No. 451-03-47/2023-01/ 200017).

## References

[1] M. Herranz, R. Idoeta, A. Mira, F. Legarda, "Calibartion frequency for gas proportional counters" *Accreditation and Quality Assurance* 12 (2007) 581-586

[2] M.R.Calin, A.E. Druker, I. Radulescu, "The calculation of the detection efficiency in the calibration of gross alpha-beta systems" *Journal of Radioanalytical and Nuclear Chemistry* 295 (2013) 283-288

[3] F. Hillenkamp, "Laser Desorption Mass Spectrometry", A Review. In: A. Benninghoven, R.J. Colton, D.S. Simons, H.W. Werner (eds), Secondary Ion Mass Spectrometry SIMS V. Springer Series in Chemical Physics. 44. Springer, Berlin, Heidelberg (1986)

[4] K. Tanaka, H. Waki, Y. Ido, S. Akita, Y. Yoshida, T. Yoshida, "Protein and Polymer Analyses up to m/z 100000 by Laser Ionization Time-of-Flight Mass Spectrometry" *Rapid Communications in Mass Spectrometry* 2 (1988) 151-153

[5] Multi Agency Radiological Laboratory Analitical Protocols Manual (MARLAP), Vol. II, Appendix F, Part II (2004)

[6] A.M. Sanchez, G.S. Garcia, M.J. Vargas, "Study of self-absorption for the determination of gross alpha and beta activities in water and soil samples" *Applied Radiation and Isotopes* 67 (2009) 817-820.

[7] Rulebook on Limits of Radionuclides Contentin Drinking Water, Foodstuffs, Feeding Stufffs, Medicines, Product for General Use, Construction Materials and Other Goods to be placed on Market (Official Gazette RS 36/18)

 ISBN 978-86-7466-970-9