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METHOD OF N-15 ANALYSIS BY MASS-SPECTROSCOPY ON ION IMPLANTER MPB-200

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ABSTRACT

The Industrial Implanted MPB-200 has been modified to a light-isotopes mass-spectrometer. Mass-resolution has been improved by combination of the quadrupole focusing system and a collimator with additional scattering shielding. Single beam method has been set up, in which mass-spectrums are obtained by scanning magnetic field of the separator. A start-stop control system has been added to operate automatically the magnet and registration system, from which signals are transferred to a XT/AT computer for saving and analysis. The mass-resolution is satisfactory for analysis of light isotopes with mass numbers A less than 40. A testing measurement has been done with standard samples of natural and enriched N-15 isotope, at acceleration energy of 50 keV, beam current less than 100 nA, vacuum of 4 x 10E-6 and collimator's shell of 1 mm. Obtained resolution and background condition allowed to achieve a good linear dependence of relative isotope ratio data vs real abundance in the range from natural (0.365%) to 5.0% with a 3% error (96% of reliability). Routine N15 analysis may achieve (5-10)% accuracy by a (7-10) minutes measurement for every sample. Sensitivity of the mass-spectrometer is better almost by one order in comparing with one of emission spectrometers. The new mass-spectroscopy system is applied to research in agriculture, biology and environmental study.

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I. INTRODUCTION

Stable N15 isotope labeled technique is a powerful analytical method for direct study of quantitative dynamically processes of protein and Nitrogen concerning substance in biology, agriculture and environment. Since 1991 an emission spectrometer NOI 6E (made in GDR) has been applied at Centre for Nuclear Techniques Application in Ho Chi Minh City for study of soil-fertilizer-plant relationship. Another Japanese emission spectrometer has been operating since 1993 at the National Institute of Agricultural Science for study of Nitrogen fixation of Rhizobium bacteria. Besides emission spectrometry, mass-spectroscopy is alternative technique with improved sensibility by almost one or two order [1]. A possible negative factor of mass-spectrometers for routine laboratory work is their high cost.

The purpose of this research is to modify an industrial ion implanter MPB-200 into a mass-spectrometer for light isotopes analysis, while keeping its ion implantation ability unchanged. The MPB-200 implanter, made in Switzerland in early 70's belonging to the Morning Star Semiconductor Company, is a linear ion accelerator with maximum energy 200 keV and beam currents of (10-100) μA for wide assortments of ions. There is a beam line system with an electric magnet and two quadrupole lenses for focusing. Acceleration high voltage and electric magnet current have high stability of 5 x 10E-4 [2]. An our preliminary study considered implanter's parameters as satisfactory for making of a mass-spectrometer for light isotopes with mass-numbers less than 40. For example of rare isotopes of Nitrogen and Oxygen, relative sensitivity may achieve 10E-4 to 10E-6 in comparison with widespread isotopes (N14 or O16) [3].

II. MASS-SPECTROSCOPY SYSTEM FOR N15 ANALYSIS

In the Fig. 1, there is a general scheme of the mass-spectrometer, based on the implanter MPB-200.

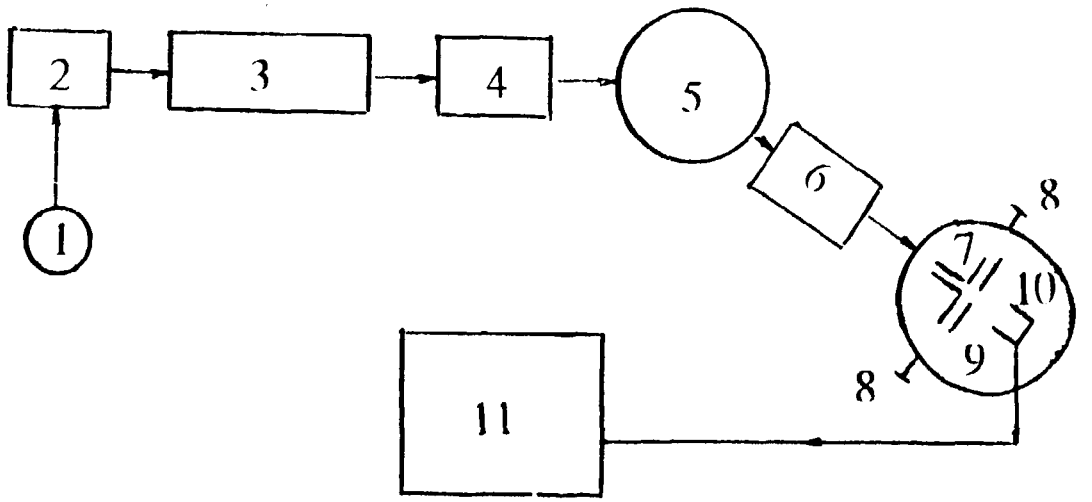

Fig. 1. Scheme of MPB-200 mass-spectrometer:
1/ Gas sample bottle; 2/ Ion source; 3/ Accelerator; 4/ Quadruple No.1; 5/ Magnet; 6/ Quadruple No.2; 7/ Beam slit; 8/ Slit regulator; 9/ Suppresser; 10/ Collector; 11/ Read-out and control system.

1. Sample inlet system and ion beam formation:

Total Nitrogen yield of a sample is determined by well-known Kjeldahl method. For N15 abundance analyzing, the obtained Kjeldahl ammonium extract was converted into Nitrogen gas by Rittenberg oxidation reaction as following [4]:

$$2\,NH_4Cl + 3\,NaOBr + 2\,NaOH \rightarrow N_2 + 3\,NaBr + 2\,NaCl + 5\,H_2O; \qquad (1).$$

The Rittenberg reaction (1) takes place under vacuum of 8x 10E-5 Torr, in a Rittenberg flask, serving as the sample bottle 1

in the Fig. 1, which is connected by an inlet system to the ion source 2. It was found that for the MPB-200 mass-spectrometer 50 microgram of Nitrogen gas is enough for an analysis. In the ion source a wolfram thermal cathode is used for ionizing gas molecules from sample bottle. In the next step ion gas is focused into the accelerator 3, which presents as a linear acceleration tube with a high voltage supply of 200 kV as maximum. At the output of the accelerator an ion beam is now formed and ready for mass-spectroscopy analysis.

2. Mass-separation:

The mass-separator consists of an electric magnet 5 and two quadrupole lenses 4 and 6. Magnet current may be regulated from 0 to 150 A, that practically includes all mass range up to A = 100. The quadrupoles No. 1 and No. 2 in combination may create a good ion beam focus in the next beam line. Width of the beam's cross-section may be regulated to (1-2) mm by changing focusing electric fields of the quadrupoles.

3. Registration and read-out system:

Analysis of isotopes as N15 requires a very good mass separation due to negative influence of neighbor strong peaks. In order to improve mass resolution a new single beam registration system is used, including a narrow slit 7 and a Faraday cup - the ion charge collector 10. Width of slit is easily changed by the regulator 8. The Faraday cup is shielded of scattering ions by metallic leaves. The suppressor 9 with negative voltage helps to avoid effects of emitted electrons. From the collector, current signals are transmitted to a current integrator of the read-out system 11. In Fig. 2 the

block-scheme shows how signals are registered and how to control a mass-spectroscopy measurement.

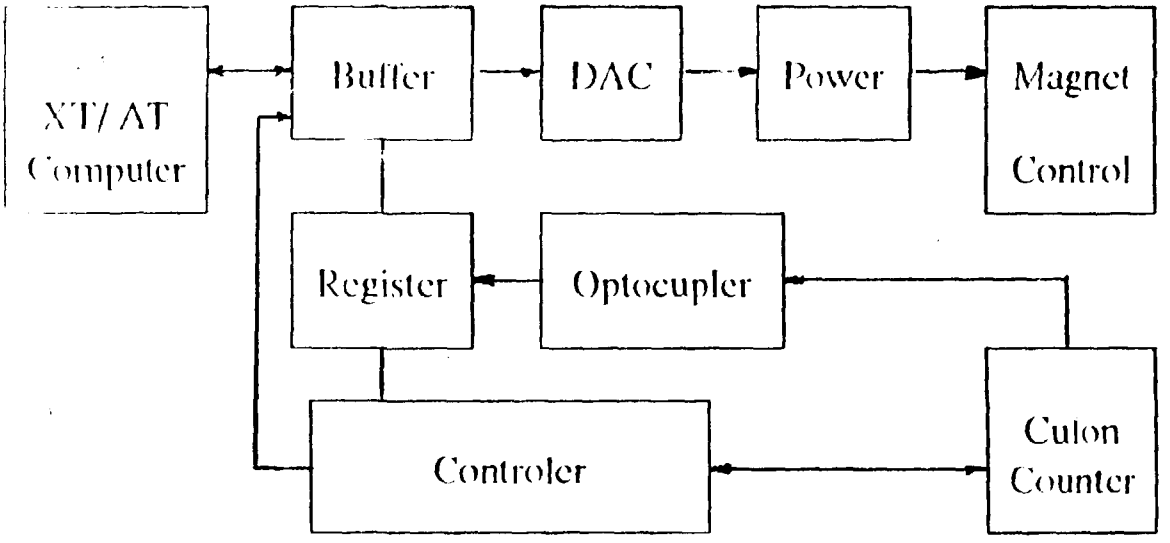

Fig. 2. Block-scheme of the registration-control system.

During operation a controller card is linked to XT/AT computer slot, which has a task to operate the separation magnetic field in a fixed range with investigated mass-peaks. When the magnet's current reaches a given investigated mass-region, the computer orders a register 74193 to start registering charge signals, coming from the current integrator. After fixed time the measurement is stopped and the registered data is transferred to the computer for saving and processing.

III. RESULTS OF N15 ANALYSIS

In the present work, standard samples with abundance from the natural value 0.365 to 5% are applied to the MPB-200 mass-spectrometer. This range includes all used in practices N15 isotope labeled ratios.

N15 isotope analysis is often realized by measuring ratio of molecular peaks 29 to 28 due to advantage of background condition in comparing with atomic peaks.

In Fig. 3 a typical obtained mass-spectrum with abundance 1.2% is demonstrated. The Nitrogen 28 is registered in a scale of 10 times greater than for Nitrogen 29 and NO (30). Background is defined by intervals (a) and (b), contributed mainly by scattering from peaks and by apparatus leaking current at a given registering scale. Besides the background, it is necessary to define the scattering queues of peaks 28 and 30 in Nitrogen 29 peak. Only after that real counts of

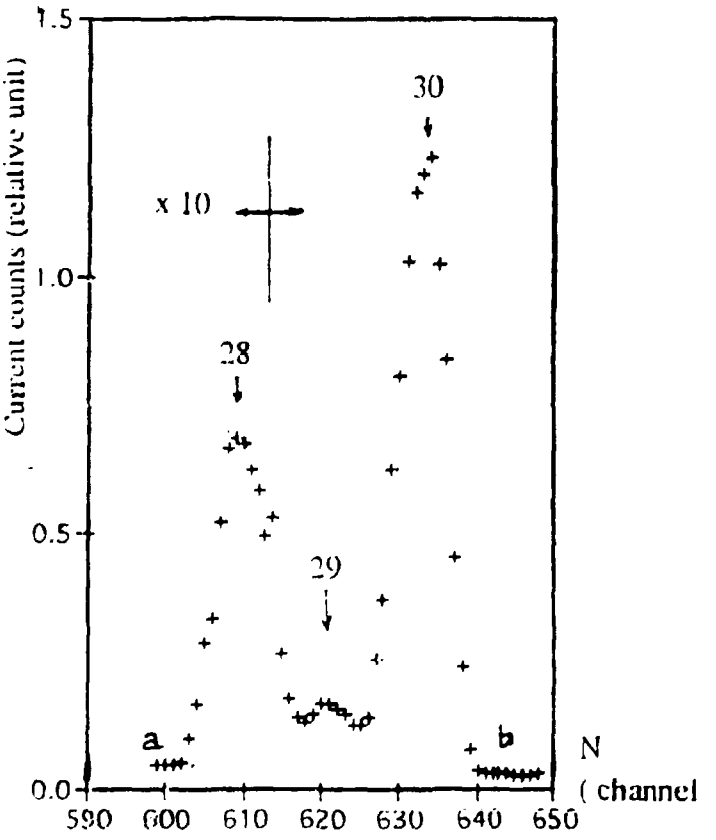

Fig. 3: Mass-spectrum of N15 isotope analysis

the peak 29 may be found for obtaining the isotopes ratio.

In the experiment 11 standard diluted isotope ratios were tested. Measurements have been done at: accelerated ion energy of 50 keV, vacuum of 4 x 10E-6 Torr., gas pressure of 1.5 x 10E-5 Torr. and ion current of 20 nA to 60 nA for the peak of Nitrogen 28. For every measurement it takes about 50 microgram of Nitrogen, which is enough for obtaining 5 to 10 repeated mass-spectrums. All procedure of Rittenberg reaction and spectrums recording took 15 minutes for every sample. Vacuum pumping and sample gasifying reaction were carried out without liquid Nitrogen freezing. Obtained experimental isotope ratios are shown in the fig. 4. Relative standard error of every point is 3% to 5%. Approximation by linear function $y = ax + b$ gives the best agreement with: $a = 0.100 \pm 0.003$ and $|b| < 0.004$ for 96% of reliability.

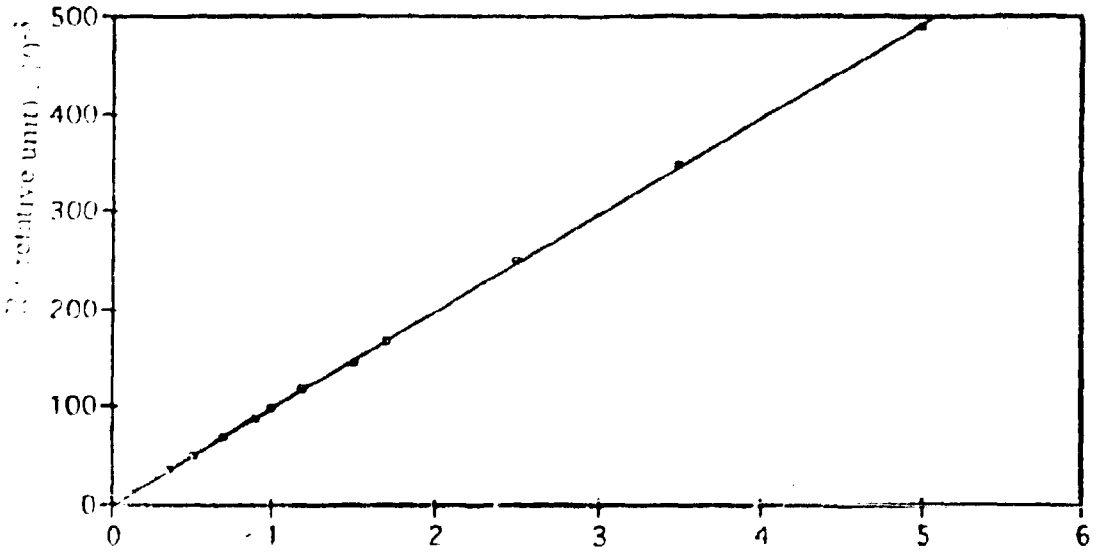

Fig. 4: Standard data of N15 isotope ratios:
points - experimental ratios; line - linear approximation.

IV. CONCLUSION

Experimental data of N15 ratios in the present work have good linear sharp with accuracy at least by 5 times better than a similar standard data of emission spectrometry recently done [4] in according to evaluation in [1]. Due to this advantage the MPB-200 mass-spectrometer may be used either for research with very low N15 isotope ratios near to the natural abundance or for calibration of other emission spectrometry N15 analyzers. The other advantage of the mass-analyzer is simple procedure of sample preparation.

Time taken for a routine N15 mass-analysis may be reduced to (7-10) minutes, in which obtained experimental isotope ratio may achieve an accuracy of 5% to 10%. This sensitivity satisfies a lot of researches in biology and agriculture.

Furthermore, the MPB-200 mass-spectrometer has still a potential to improve its sensitivity by one or two order in isotope ratio analysis, which is appreciable for hydrological and environmental study.

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