

# Design, characteristics and scientific tasks of the LASMA-LR laser ionization mass spectrometer onboard Luna-25 and Luna-27 space missions<sup>†</sup>

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## ARTICLE INFO

### Article history:

Received 15 December 2020

Received in revised form

3 May 2021

Accepted 19 July 2021

Available online 21 July 2021

### Keywords:

LASMA

Laser ionization mass spectrometry

Element composition

Isotope composition

Regolith

Time-of-flight mass spectrometry

## ABSTRACT

The laser-ionization time-of-flight mass spectrometer LASMA-LR is part of the scientific payload of the Luna-25 and Luna-27 missions. The instrument is able to perform analysis of elemental and isotopic composition of solid samples (regolith and dust) with high accuracy and high spatial resolution. The principle of the instrument operation consists in complete atomization and ionization of the substance by a laser pulse, separation of ions during their free expansion, depending on their mass and charge, and subsequent registration of the ions time of flight from the sample to the detector. The instrument has small dimensions (130 × 206 × 254 mm), low weight (2.8 kg) and low mean operating power consumption (8 W). The limits of detection for element analysis are at least 50 ppm (ppm atomic fraction) in one mass spectrum and 5 ppm at analysis of an accumulation of 100 mass spectra. The scientific data which will be obtained by LASMA-LR can be essential for a wide range of studies, such as the geological characteristics of spacecraft landing sites, analysis of the lunar dust composition, search for rare earth elements, native metals and alloys, determination of the content of chemically bound water in regolith, and others. Achievement of these tasks will contribute to the study of fundamental questions ranging from the formation and evolution history of the Moon to the advancement of a number of applied problems of the Moon exploration and colonization.

With the LASMA-LR instrument we have demonstrated that it is possible to provide all these analytical capabilities in a very compact, lightweight and at low power, which lends itself to operational concepts not only for robotic probes landed on the Moon, but also for proposed human spaceflight missions to the Moon and robotic missions to asteroids for the local prospection of mineral resources with a portable device, possibly as equipment carried by astronauts during their surface missions.

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## 1. Introduction

Laser ionization time-of-flight mass spectrometry (LIMS) is considered like one of the most promising approaches for elemental, isotopic, and molecular analyses of the solid substances in space experiments [1–5]. This is due to the relative simplicity of construction and robustness of LIMS instruments in combination with high accuracy and high spatial resolution. LIMA-D was the first flight laser ionization mass spectrometer and it was onboard

Phobos-1 and Phobos-2 missions [6, 7, 1]. The instrument was able to perform distant (up to 70 m far) analysis of elemental and isotopic composition of the Phobos' regolith. Despite the failure of the Phobos missions, the development and improvement LIMS instruments was continued. As a result, laboratory prototypes were developed in several laboratories [2,3,8,9] and the flight model of the laser ionization mass spectrometer LASMA was constructed [1]. LASMA was aimed to perform direct (not remote) analysis of regolith, had a smaller mass and size than the LIMA-D, and had 100 times higher sensitivity and 2 times higher mass resolution [10,1].

The LASMA mass spectrometer was included into the complex of scientific equipment of the Phobos-Grunt mission [11, 1, 12]. It was aimed to study element and isotope composition of Phobos regolith and basing on these data to classify minerals of the Phobos'

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regolith, to assess the regolith heterogeneity, to study isotope composition, etc. It would have contributed significantly to the knowledge on the origin and evolution of Phobos. Unfortunately, the Phobos-Grunt spacecraft failed, and the scientific investigations on Phobos' surface could not be performed. Nevertheless, in the course of laboratory and pre-flight tests, the LASMA instrument had proven itself well.

Along with the mentioned advantages of the LIMS method, this led to the inclusion of a LASMA-type instrument, named LASMA-LR, which differs from the instrument on Phobos-Grunt [1] and the earlier prototypes in the modification of some units, to the scientific payload of the Luna-25 and Luna-27 missions [13]. LASMA-LR has been designed and developed between 2011 and 2018, and flight units and flight spares units for the Luna-25 all have been delivered, while for the Luna-27 the flight instrument have been constructed and flight spares units are under production. The launch of Luna-25 is scheduled for October 2021 and the launch of Luna-27 is foreseen for the year 2025. The main tasks of these missions are to develop the technology of soft landing in the circumpolar region of the Moon, to develop the technology of long-term operation on the lunar surface with the experience of a lunar night, to study the composition and structure of the regolith and to study the lunar exosphere. Through the missions, LASMA-LR main goal is to provide general characteristic of the regolith in the landing sites.

## 2. Scientific tasks

The laser time-of-flight mass spectrometer LASMA-LR is able to determine the elemental and isotopic composition of the regolith at the landing sites of the Luna-25 and Luna-27 missions. Such data can be implied for a wide range of scientific tasks. In particular, geochemical classification of the Lunar rocks is possible basing on concentrations and ratios of some chemical elements and oxides, including Fe, K, Al, Mg, Ti, etc. [14,15,16]. The data on elemental composition also would allow to identify minerals within the regolith [17,18]. The content of elements implanted into the regolith by the solar wind - H, C, N, He, Ne, Ar, Kr, Xe - is one more important characteristic of the regolith [15,19], of which a fraction is released into the lunar exosphere [20]. The content of the more abundant of these elements can be measured by LASMA-LR. The combination of data on the characteristics above will contribute to the understanding of the geological history of the landing sites rocks and to the space weathering factors (meteorite bombardment, solar wind intensity) that affected the surface through geological time. The Luna-27 mission is equipped with a drilling device allowing to access samples down to ~1 m below the surface [21,22]. So, a depth-by-depth analysis of the regolith is possible, which will allow a more detailed reconstruction of the landing site geological history.

Data on the elemental composition of lunar rocks are essential to study the formation of the Moon. Wherein, special attention should be paid to vapor-mobilized elements (VME): F, S, Cl, Cu, Zn, As, Se, Br, Ag, Cd, In, Te, I, Hg, Tl, Pb, Bi. Comparison of these elements' concentrations with the ones in terrestrial rocks helps to understand whether the Moon and the Earth originated from the same material, and to reveal the temperatures of their accretion. Through the excess of VME the amount of meteorite material presented in the sample can be approximately estimated, and the ratios of the elements allow to determine the chemical diversity of the meteorites responsible for this excess [15,23].

It should be noted that in spite of a number of earlier missions to the Moon, which delivered regolith and rock samples to the Earth, as well as intensive remote sensing of the Moon, data on the chemical composition of the regolith are still incomplete. A striking example of this is the results of the LCROSS experiment, in which unexpectedly high concentrations of mercury (1.2 %) and carbon

monoxide (5.7 %) were found in the lunar rocks [24,25]. In the South polar region of the Moon, where the Luna-25 and Luna-27 landing sites are planned [26], mainly remote sensing was carried out [27,28]. The direct analysis of the lunar regolith chemical composition by Luna-25 and Luna-27 not only will provide more detailed characteristics of the lunar soil, but also will allow for the calibration and interpretation of remote sensing data [29]. Remote studies of the South polar region of the Moon suggest high water content (about 5 %) in the regolith [27]. However, it is unclear if this water is in the form of water ice, or if it is in a mixture of ice with mineral particles, or in a chemically bound form within minerals [30,31,27]. Measuring the hydrogen content in the regolith using LASMA-LR will allow to approximately assess the amount of bound water (meaning the hydrogen content), since the ice in the sample should sublime quickly when loaded into the sample-receiving unit of the device.

Minerals that are rare on the Earth or previously unknown in nature, native metals, and alloys found on the Moon are great of interest [32,33,34,35]. These findings indicate the existence of previously unknown mechanisms of mineral formation. Particle sizes of such minerals and alloys commonly are from hundreds of nanometers to tens of micrometers. Taking into account the diameter of the LASMA-LR instrument laser spot (30  $\mu\text{m}$ , see below), the detection of unusual mineral phases is possible by analyzing individual spectra.

There is a range of tasks associated with the possible creation of lunar bases and the Moon industrial development. Over the years, the idea of creating a base on the Moon has been gaining relevance: economic assessments are being carried out, new materials and technologies are being developed, research is being performed on possible sites for creating such a base [36,37,38,39]. For future mission, considering the capabilities of LASMA-LR with a compact and low power instrument, that can easily fit into the equipment for astronauts to carry it around and do *in situ* science with a small portable laboratory.

The data on the content of rare Earth elements in the lunar regolith contribute to a correct assessment of the prospects for its industrial exploitation [40]. Data on the chemical and mineralogical composition can be useful for studying the possibility of plants growing within the lunar base and creating any materials from the regolith [19, 41, 42]. An important aspect of lunar research from the point of view of its exploration is the study of lunar dust, since it can pose danger to spacecraft, instruments, and humans [43, 44, 45]. In this regard, the LASMA-LR instrument will be able to perform the element analysis of the dust that will be deposited on the sample-receiving unit after the landing of the spacecraft.

## 3. Principle of the instrument operation

The principle of operation of the laser time-of-flight mass spectrometer LASMA-LR is the same as that of the LASMA instrument on Phobos-Grunt [1]. LASMA-LR consists of the following elements: a regolith sample is placed in one of the cavities on a rotating disk that is at a distance corresponding the focal length of the laser emitter, after which a 7 ns laser pulse with a power density of  $\sim 10^9 \text{ W/cm}^2$  is applied to the sample. The impact of the laser pulse leads to complete atomization and ionization of the ablated material from the sample substance, its strong overheating and, as a consequence, the emission of the formed ions in the form of a plasma torch. High-speed ions emitted from the resulting plasma in the free-expansion mode enter the time-of-flight mass analyzer, where they are separated by time of flight in accordance with the formula:

$$T = L \times (M/2E)^{1/2}$$

where  $T$  is time of flight of the ion;  $E$  is the energy of the ion;  $M$  is the mass of the ion;  $L$  is field-free distance. The ions separated in time are reflected in the retarding field of an electrostatic ion reflector and then registered by a micro-channel plate (MCP) detector. Then the signal goes through a two-channel amplifier to a high-speed analog-to-digital converter (ADC), is recorded as a time-of-flight spectrum by the field-programmable gate array (FPGA), and is stored in the device memory as a single spectrum (Fig. 1).

The mass of ions can be determined from their flight time. Analysis of the mass and distribution of the areas of the isotope peaks allow to identify a chemical element. Further, according to the areas of mass peaks of elements, it is possible to determine the chemical, including elemental and isotopic, composition of the investigated substance. Based on the analysis of the ratios of mass peaks areas of individual elements, according to the corresponding data of preliminary calibrations included in the library of reference mass spectra, it is possible to determine the minerals from which the mass spectrum registered by the instrument could be obtained. By operating at optimal laser ablation conditions, the laser ion source allows simultaneously to provide an almost equiprobable output of all elements in the sample, therefore, their equally probable registration with high throughput of the mass analyzer [46]. However, taking into account the differences in the energy of the formed ions for different elements, as well as the fact that LASMA-LR registers only ions with energies of about 60–75 eV, the

quantitative measurement of the sample composition requires the introduction of calibration coefficients for each element (coefficients of relative sensitivity, RSCs, see below).

#### 4. Design and technical characteristics

Structurally, the LASMA-LR instrument is in the form of a single unit (Fig. 2, right), which includes the following main units: an electronics module (University of Bern, Switzerland), an mass analyzer (Space Research Institute of RAS, Russia), a laser emitter module with a laser focusing system (laser optical module) manufactured by the POLYUS Research Institute of M.F. Stelmakh Joint Stock Company (Russia), a power supply and control unit for a laser emitter and a sample receiving device (Space Research Institute of RAS, Russia) (Fig. 2, left). The dimensions of the instrument are  $130 \times 206 \times 254$  mm, the weight is 2.8 kg, and the average operating power consumption is 8 W.

The electronics module (Fig. 3) provides full control over the operation of the mass spectrometer, registration, storage and transmission of spectral data and telemetry, and also provides power to all units of the instrument. The registration system includes a 2-channel (14-bit, 100 MHz) ADC with analog pre-amplifiers connected directly to the MCP detector outputs with gains of 5 and 50. The simultaneous usage of two channels allows parallel registration of matrix elements and impurities with a dynamic range of more than  $10^4$ . It also increases reliability, since the

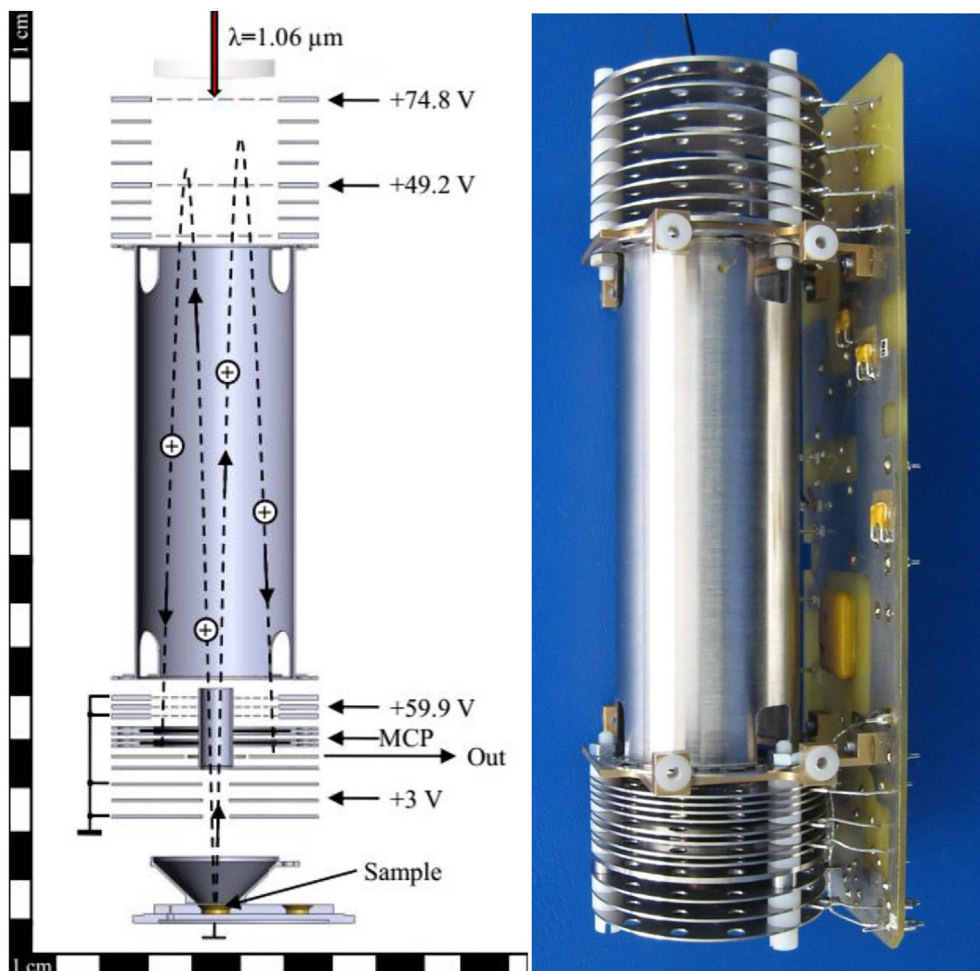
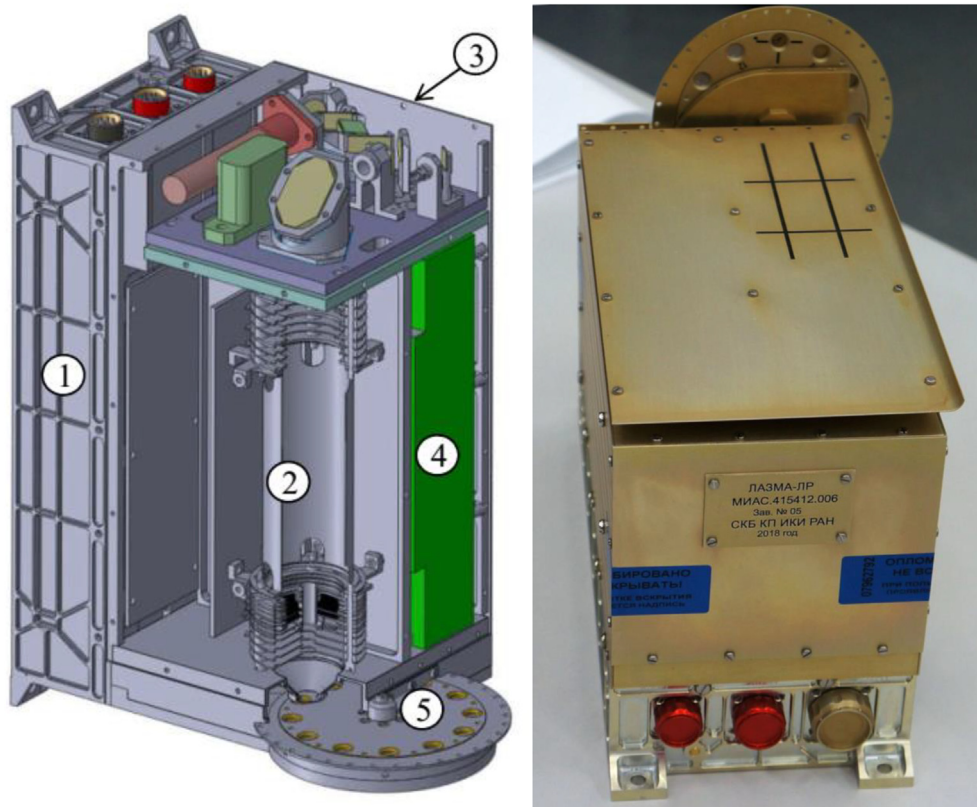


Fig. 1. Schematic diagram of the LASMA-LR instrument (left) and view of the mass-analyzer of the flight instrument (right). MCP – micro-channel plates.





**Fig. 2.** Construction of the LASMA-LR instrument, main units. Left: 1 – electronics module; 2 – mass analyzer; 3 – laser emitter module with focusing system (laser optical module); 4 – unit of power supply and control of the laser emitter; 5 – sample receiving unit; right: photograph of the LASMA-LR flight unit.

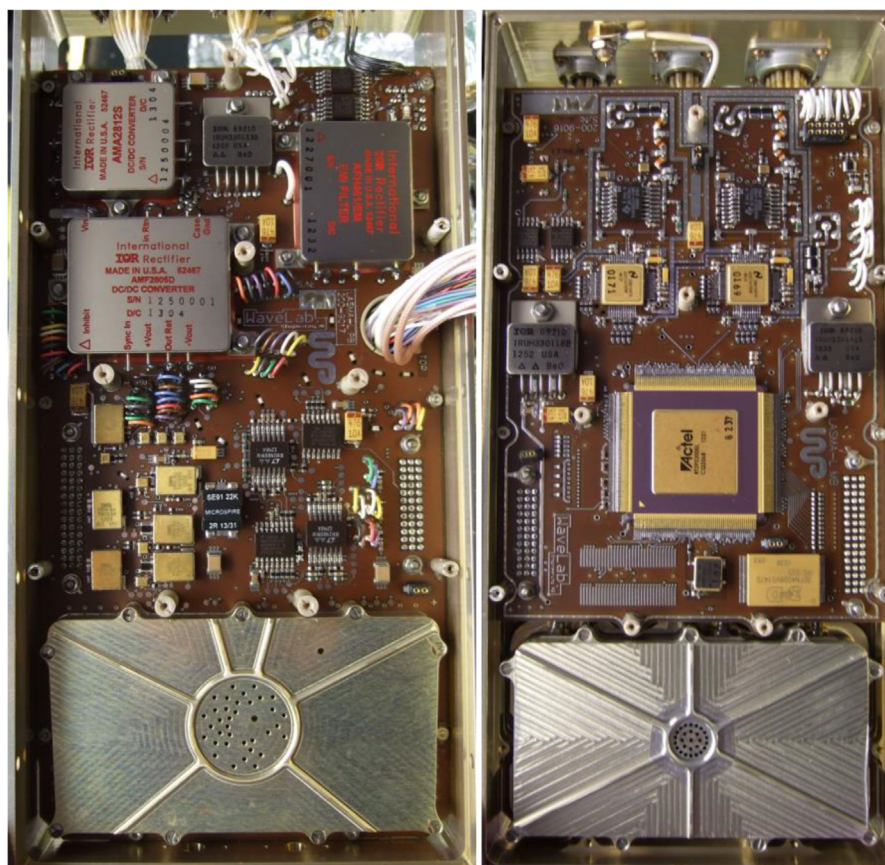
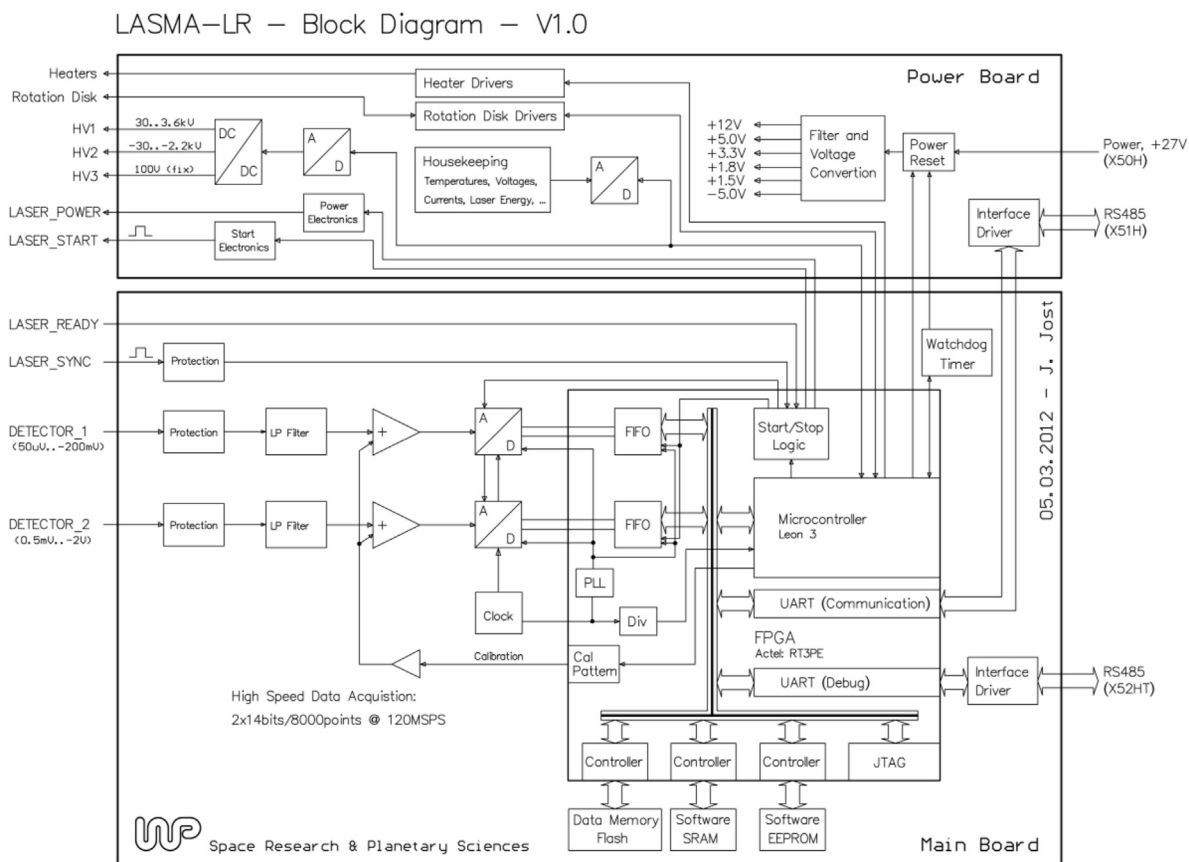
failure of one of the channels will not lead to a complete loss of the instrument's performance. The power supply system of the electronics unit, in addition to providing the units of the mass spectrometer with low-voltage power, has 3 high-voltage channels for powering the optical attenuator, analyzer grids, and MCP. The electronics module and the entire instrument are powered by the onboard power supply system of the spacecraft with a voltage of 27.5 V. The electronics module has a built-in RS-485 interface, through which the instrument operation control and scientific information transmission are realized.

The mass analyzer has an axisymmetric design and consists of an electrostatic ion reflector and a detector. The ion reflector provides the time-of-flight focusing of ion packets onto the detector plane and allows obtaining high mass resolution while keeping all the other advantages of the instrument, like high transmission of all ion species and robust operation. The ion reflector is powered by a stabilized voltage source of 100 V (200  $\mu$ A). The detector is a chevron assembly of two microchannel plates MCPO 32-15 TSO (Baspik, Russia). MCPs have an outer diameter of 32.7 mm and an opening with a 7.5 mm diameter, a thickness of MCPs is 0.5–0.7 mm, a channels' diameter is 14.5–15.5  $\mu$ m and a channels' tilt angle is 5–9°. The detector is powered by a high-voltage from –1000 to –2200 V (200  $\mu$ A in operating mode), which permit to operate below the saturation threshold of the plates with a total gain of  $10^6$ . The geometric and electrical design of the mass analyzer, having a minimum size of  $14 \times 4 \times 4$  cm and weight about 200 g, led to efficiently collect the ion packages formed in the laser source and eventually register the ions on the detector.

The laser emitter module (Fig. 4) with a focusing system includes: Nd:YAG laser with a wavelength of 1.06  $\mu$ m, an optical system consisting of a focusing lens, and a laser radiation

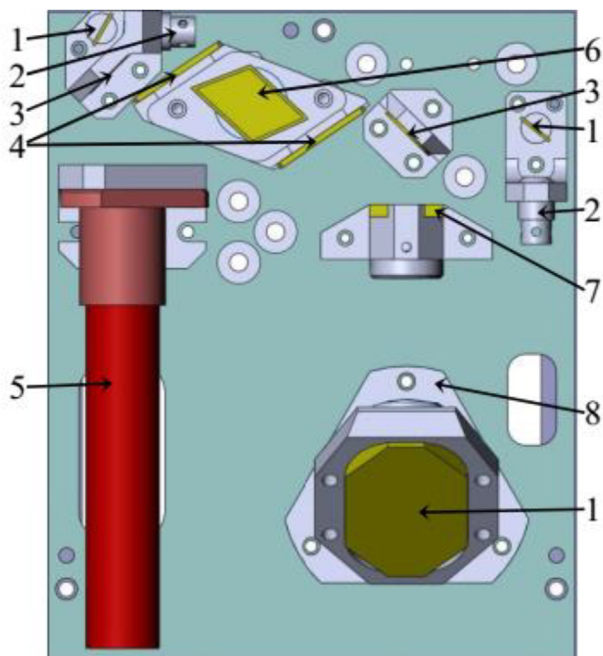
attenuator. The passively Q-switched Nd:YAG laser provides an output energy of 15 mJ with 7 ns pulse duration. Divergence of laser radiation at the laser output is 3 mrad, laser energy reproducibility is about 10 %. The maximum laser frequency is 0.1 Hz, limited by the recharging of the flash lamp of the laser and passive cooling regime of the laser. The laser performance is maintained in a wide temperature range from –50°C to +50°C. The service life is not less 100,000 shots. There are data on the better stoichiometric representation of the samples and better crater morphology at application of the lasers with shorter wavelengths [47–49]. But a low-frequency 1.06  $\mu$ m-wavelength Nd:YAG laser with relatively short service life was used, since its average energy consumption is low, it does not require active cooling in a space experiment (under vacuum conditions), and the technology of fabrication of such lasers for challenging operating conditions is well-proven. Reducing the wavelength, i.e., transition to any harmonic, would require the installation of additional nonlinear optical crystals, their thermal stabilization in a narrow temperature range, their very accurate alignment, which would significantly complicate the design and lead to an increase in power consumption. In addition, the transfer of this laser to the harmonics could lead to a decrease in the energy of laser radiation (due to a decrease in efficiency) to such a level that it would not be sufficient for ionization of the sample. Thus, the conversion of this laser to another wavelength would require the development of a novel optical module.

The optical system (Fig. 4) performs adjusting the energy and spatial characteristics of laser radiation to the sample surface. The laser radiation, linearly polarized parallel to the optical plate, is reflected from the swivel mirror and enters the electro-optical attenuator unit. The laser radiation attenuator is an electro-optical shutter based on a lithium niobate crystal. The



**Fig. 3.** LASMA-LR electronics. Top panel: block diagram of LASMA-LR electronics; bottom panel - electronics module: left – power board, right – main board.





**Fig. 4.** Design drawing of the laser optical module: 1 - reflective mirror, 2 - laser energy control unit, 3 - swivel mirror, 4 - polarizer, 5 - laser, 6 - electro-optical crystal, 7 - neutral filter followed by negative telescope lens, 8 - telescope focusing lens location.

attenuator's polarizers are designed for maximum transmission in the absence of a supply voltage across the crystal. When a half-wave voltage of 3400 V is applied to the crystal, the polarization of the laser radiation is rotated 90° and locked by the second polarizer. As a result, the maximum attenuation of the output radiation is up to 40 dB. Adjusting the voltage on the crystal allows to adjust the output laser energy according to a sinusoidal law. After exiting the attenuator unit, the radiation reflected from the second rotary mirror is directed to the telescope unit at the entrance of which there is a neutral optical filter, which roughly adjusts the laser energy to provide the required intensity range in the focal spot. The telescopic system provides focusing of the output laser radiation to a 30  $\mu\text{m}$  spot at a power density of  $10^9 \text{ W/cm}^2$  at a focal length of 180 mm. Swivel mirrors have 1 % transmission to output part of the radiation into the measuring channels, which allow monitoring the radiation energy at the output of the laser and attenuator. Thus, it is possible to precisely tune the laser ion source to obtain singly charged ions, as well as to compensate the thermal changes in the laser energy of the emitter. During development, the 30  $\mu\text{m}$  spot size was found to be optimal in terms of the quality of the ion beam. An increase in the spot size and at the same laser power density would lead to an increase in the space charge of the resulting ion beam, which, taking into account the small drift length of the mass analyzer, would lead to a deterioration of ion focusing and, as a consequence, to a critical degradation of the mass resolution. With a decrease in the focusing diameter, and at the same laser power density, mass peaks corresponding to molecular species will be observed in the mass spectra, which will complicate the subsequent analysis of the sample elemental composition. Thus, this spot size is optimal from the point of view of time-of-flight mass spectrometry and allows to analyze the composition of inhomogeneities on the sample surface with 30  $\mu\text{m}$  resolution, which can provide additional information on the regolith homogeneity.

The laser emitter power supply and control unit (UPKLI) form the high-voltage power supply of the laser emitter and carries out

telemetric control of its energy characteristics. In addition, the UPKLI generates a synchronization signal to start the sweep of the registration system. The UPKLI control is carried out according to the command sequence generated by the instrument's electronics module.

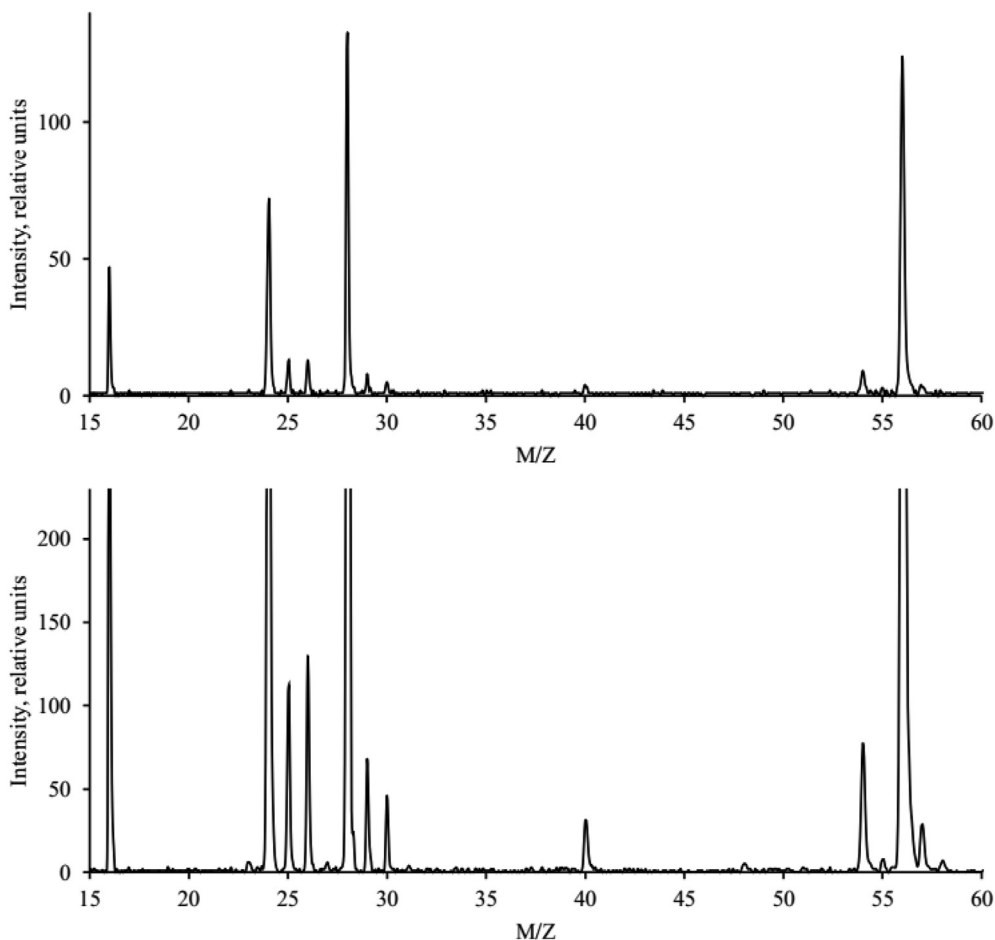
The sample receiving unit is a disk with 12 holes and is intended for fixing and introducing samples into the area of exposure to laser radiation and moving them during the analysis. The number of holes is limited by the disk (and the whole instrument) size. The presence of 12 holes allows the analysis of 11 samples taken on the surface of the Moon, since one hole is occupied with a reference sample. Since the Luna-25 and Luna-27 missions are landers (not rovers), it is suggested, that such limitation of the samples' number will not crucially interfere the landing sites characteristic. After loading the regolith by the spacecraft manipulator into the receiving hole of the unit, on command, it is moved to the area of laser pulse. When moving, excess regolith is dumped, and the sample is compacted so that the plane of the sample analyzed is in the focal plane of the laser optical system. After the sample preparation, during the analysis, the sample is periodically shifted by 50  $\mu\text{m}$  to eliminate the effect of the crater on the formation of plasma, as well as to study the entire surface of the sample. Analysis of up to 80 points is possible on the sample surface before reversing movement (i.e. before edge of the sample will be reached). There is a play during the disk movement, and the surface of the sample rubs against the diaphragm of the instrument, which excludes the laser spot hitting the previously formed crater. The control of the disc positioning process is carried out using Hall effect sensors.

The reference sample is MC146 alloy, containing W, Ti, Ta, Nb, Co, and C in concentrations 28.24, 4.79, 2.27, 1.30, 26.80, and 36.60 at.%, respectively. The choice of this material as a reference is due to the content of elements in a wide range of masses, the strength of the material (the ability to withstand vibration and shock loads), its monolithic (rather than loose) structure, and the shallow depth of the crater formed at the laser shot, which allows laser shots at one depth for a long time without degradation of spectral characteristics.

## 5. Analytical characteristics and calibration

The laser ionization time-of-flight mass spectrometer LASMA-LR allows the analysis of ions in a wide range of masses – 1–250 a.m.u. (Fig. 5). Mass resolution ( $M/\Delta M$ ) is 300, absolute mass detection limit at analysis of one spectrum is  $5 \times 10^{-14} \text{ g}$ , dynamic range of one spectrum is  $10^4$  (and is limited by ADC dynamic range and noises in the instrument), elemental analysis accuracy for matrix elements when analyzing an array of 100 mass spectra is not less than 10 %. Laboratory analyzes of various analogs of regolith, rocks and minerals have shown that the limit of detection of elemental analysis is at least 50 ppmA in one spectrum and 5 ppmA when analyzing the accumulation of 100 mass spectra. In heterogeneous samples, it is possible to detect elements with even lower bulk concentration thanks to the very small size of the laser spot. It is important that the instrument allows analysis with a spatial resolution of 30–50  $\mu\text{m}$  due to the sample positioning system and the small size of the laser spot. In addition, layer-by-layer analysis of a sample to a depth of 10  $\mu\text{m}$  is possible with a thickness of each analyzed layer up to ~1  $\mu\text{m}$  depth. It allows to analyze local sample inhomogeneities on a microscale.

The accuracy of element and isotope composition analysis using LASMA-LR mass spectrometer depends significantly on the number of spectra analyzed and thus, in fact, on the number of ions sampled. Previously, relative standard deviations (RSDs) of elements concentrations for various volumes of the spectral array (mass spectra from same sample) were assessed [50]. The less RSDs



**Fig. 5.** Mass spectrum of enstatite obtained using LASMA-LR instrument. The two panels represent the same mass spectrum, but for two registration channels different in sensitivity.

were observed for elements with high concentrations in the sample, which is common for LIMS [51,52]. At analysis of 300 spectra, 10 % RSDs were achieved even for impurity (minor) elements (Fig. S1). At analysis of a similar spectral array, 1 % RSDs in measuring isotope abundances were achieved, but only for isotopes in a ratio of no more than 10:1. Achieving similar RSDs for isotopes with higher ratios requires the analysis of unreasonably large spectral arrays (thousands and tens of thousands of spectra). In this regard, a way to increase the accuracy of the isotope ratios analysis during the Luna-25 and Luna-27 missions has been proposed. As mentioned above, the sample receiving unit of the instrument allows analysis of 11 regolith samples. Assuming that the inhomogeneity of isotope ratios in samples taken at a short distance should be absent, the analysis of isotope distributions for isotopes with low concentration is planned to be carried out according to the summary statistics obtained from all the samples analyzed. It is estimated that such approach will allow to characterize with 1 % accuracy the isotopic distributions for nuclides with ratios of their abundance in nature of 50:1 or more [50]. Despite that the instrument does not have any specific scientific tasks for measuring isotope ratios during lunar missions, isotope data will be obtained along with information on the element composition and can be used in the future.

Due to differences in the ionization energy of chemical elements and due to heterogeneity of the laser energy absorbance by samples with different characteristics (e.g. color, form of the surface), LIMS analysis is affected by a systematic error [53,54]. This error is

corrected by introducing calibration coefficients, termed the relative sensitivity coefficients (RSCs). For Lunar regolith's analysis by the LASMA-LR instrument in the course of the space missions, the following operation sequence is foreseen:

- 1) obtain Lunar regolith mass spectra;
- 2) define the type of the mineral/rock (e.g. [17,18]) based on the qualitative (not quantitative) data on the sample's elemental composition;
- 3) analyze Earth's mineral/rock of the same type (and having the elemental composition characterized by any methods of analysis, i.e. standard certified samples) using an analogous laboratory model of the LASMA-LR instrument (ground reference model);
- 4) calculate the RSCs based on the spectra obtained in the laboratory;
- 5) re-analyze the data obtained by the flight instrument with the application of the RSCs calculated above.

The assessment of the instrument accuracy with application of the sequence close to above was performed. An enstatite sample (a mineral found in meteorites and lunar regolith) previously characterized with energy-dispersive X-ray spectroscopy (EDS) [50], was analyzed with the ground reference model of the LASMA-LR instrument. An array of 600 spectra was obtained. The data on chemical composition obtained by EDS were considered as a reference. The RSCs were calculated for the spectral array. Further

**Table 1**

Characteristics of the LASMA-LR accuracy obtained at elemental analysis of enstatite. Sr –relative standard deviation.

| Element | Concentration found by EDS, at. % | RSCs  | Concentration found by the flight instrument with application of RSCs, at. % | Relative error, % | Sr+ (overestimates), % | Sr- (underestimates), % |
|---------|-----------------------------------|-------|------------------------------------------------------------------------------|-------------------|------------------------|-------------------------|
| Al      | 0.034 ± 0.004                     | 3.427 | 0.027                                                                        | 19.7              | 19.3                   | 17.6                    |
| Ca      | 0.108 ± 0.011                     | 3.064 | 0.120                                                                        | 10.9              | 7.4                    | 5.5                     |
| Cr      | 0.003 ± 0.003                     | 4.164 | 0.002                                                                        | 9.9               | 16.3                   | 14.6                    |
| Fe      | 2.881 ± 0.029                     | 4.017 | 2.813                                                                        | 2.4               | 7.6                    | 6.5                     |
| Mg      | 17.028 ± 0.068                    | 0.763 | 16.576                                                                       | 2.7               | 3.5                    | 2.2                     |
| Mn      | 0.012 ± 0.006                     | 3.084 | 0.015                                                                        | 23.5              | 8.0                    | 6.2                     |
| Na      | 0.007 ± 0.004                     | 3.949 | 0.009                                                                        | 34.9              | 13.5                   | 11.7                    |
| O       | 59.978 ± 0.014                    | 0.041 | 60.369                                                                       | 0.7               | 5.6                    | 6.7                     |
| Si      | 19.937 ± 0.052                    | 1.000 | 20.053                                                                       | 0.6               | 6.3                    | 3.3                     |
| Ti      | 0.013 ± 0.007                     | 8.627 | 0.016                                                                        | 23.1              | 11.5                   | 9.6                     |

these RSCs were applied for analysis of the spectral array (135 spectra) obtained for the same enstatite sample using flight instrument (Table 1).

The resulting mean values of the matrix elements (O, Si, Fe, Mg) defined basing on the 135 spectra differ from the reference values less than in 3 at.%. The standard deviations of the contents of these elements were within 8 at.%. The lowest accuracy was observed for Na, for a difference with the reference value of about 35 at.% at an Na content in the sample of about 70 ppmA. It is obvious that the decrease in the measurement accuracy for impurity elements is primarily due to the inhomogeneity of their spatial distribution [51, 52, 50]. The accuracy can be increased by accumulation of a higher number of spectra, but the limited resource of the laser, the frequency of laser operation, and the operational constraints of the mission should be taken into account (see Design and technical characteristics section and [50]).

The experiment above does not fully reproduce the operation sequence since the same sample was used for analysis by laboratory and flight instruments. Therefore, the accuracy was additionally assessed by analyzing two bauxite samples (supplied by Alcoa, USA). Firstly, NBS69B sample was analyzed by the laboratory instrument, and based on these measurements the RSCs for each chemical element were calculated (Table 2). Further, the SRC-1 bauxite sample was analyzed by the flight instrument, and the RSCs obtained for NBS69B sample were applied for the data analysis. The spectral arrays analyzed were about 100 spectra for each instrument. We found, that the relative error was within 7 % for the matrix elements with atomic concentrations above 1 %. The RSDs for the same elements were within 8 %. The highest relative error

(88.6 %) was obtained for P, for which the abundance in the sample was about 0.07 %. It should be noted, that some elements (V, Cr, Zr, Ca), not certified in the SRC-1 sample, were found by LASMA-LR, and some elements (Zn, Mg) certified in NBS69B sample like minor components (up to 0.06 at.%) were not revealed by laboratory LASMA instrument. Such differences can be explained by inhomogeneity in the spatial distribution of minor elements, as indicated above, or by insufficient volume of spectral array.

The data presented confirm the possibility of application of the suggested operational sequence. At the same time we note that the factors that affect the RSCs involve the particular sample heterogeneity, laser absorbance, sample morphology, etc. The available identified terrestrial samples may have little or no similarity to the lunar samples for these factors. Due to that studies on the influence of the factors mentioned above as well as creation of local base of calibration spectra are planned for correct data interpretation.

## 6. LASMA-LR operation during Luna-25 and Luna-27 missions

LASMA-LR will be off during cruise. After landing, it will be commissioned by measuring a pre-loaded calibration sample. Then, the instrument will be ready to accept lunar soil delivered by the spacecraft manipulator to its sample-receiving unit.

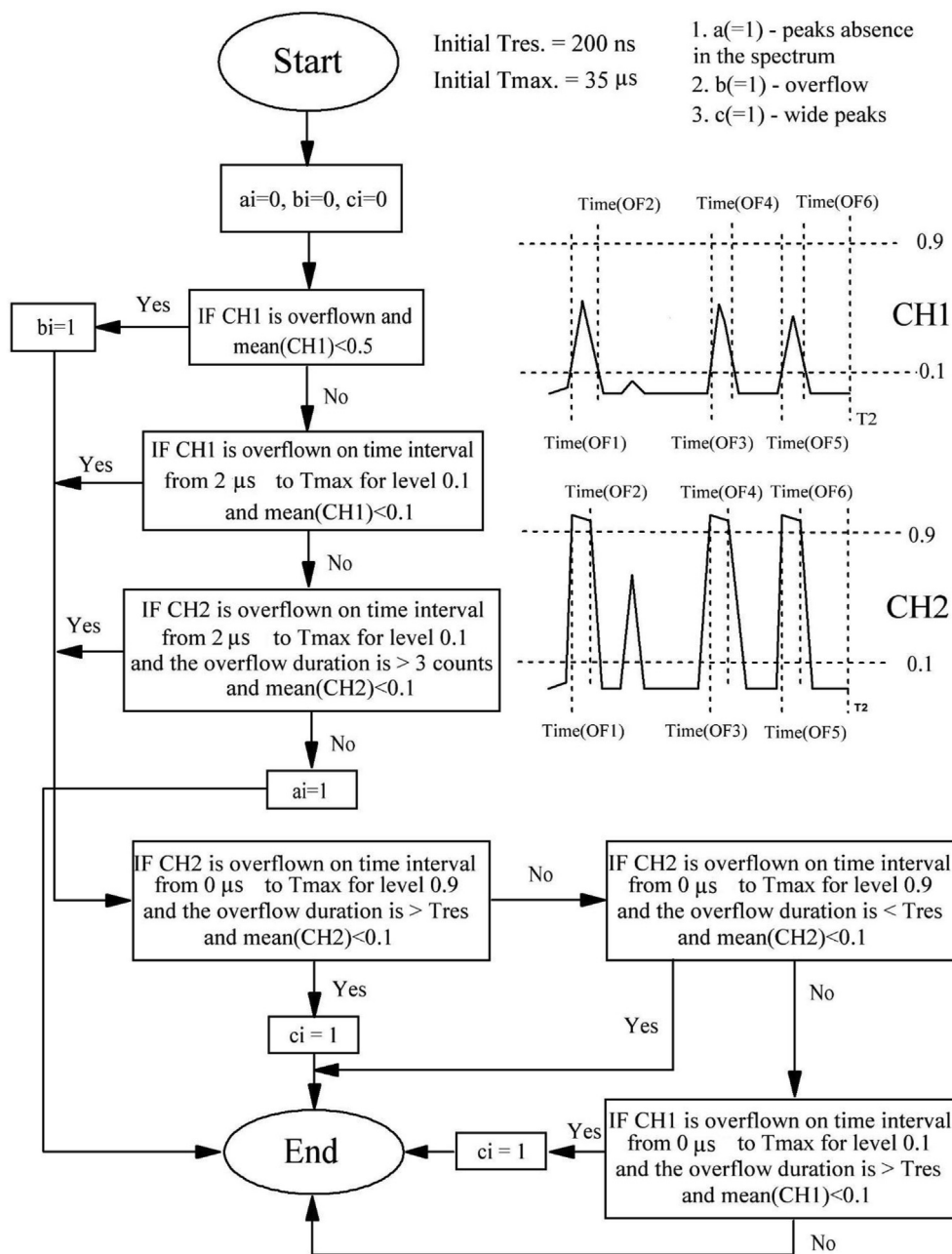
As indicated above, the sample receiving unit allows loading 11 regolith samples. The loading and analysis of samples can be performed in an arbitrary sequence “loading one sample for individual analysis” or “load all samples for subsequent batch analysis”. It is also possible to analyze the dust passively deposited on the sample receiving unit of the LASMA-LR instrument after the spacecraft

**Table 2**

Characteristics of the LASMA-LR accuracy obtained at elemental analysis of two bauxite samples with reproduction of operational sequence of data analysis suggested for lunar mission.

| Element | NBS6B, certified concentration, at. % | NBS6B, concentration found without RSCs application, at. % | RSCs  | SRC-1, certified concentration, at. % | SRC-1, concentration found by flight instrument with RSCs application, at. % | SRC-1, relative error, % | SRC-1, RSD, % |
|---------|---------------------------------------|------------------------------------------------------------|-------|---------------------------------------|------------------------------------------------------------------------------|--------------------------|---------------|
| Si      | 6.55                                  | 13.84                                                      | 0.81  | 6.07                                  | 6.29                                                                         | 3.5                      | 6.35          |
| Fe      | 2.61                                  | 12.34                                                      | 0.36  | 1.98                                  | 2.11                                                                         | 6.4                      | 6.94          |
| Ti      | 0.69                                  | 4.48                                                       | 0.27  | 0.71                                  | 0.89                                                                         | 25.4                     | 10.58         |
| Al      | 28.00                                 | 47.92                                                      | 1.00  | 29.27                                 | 29.86                                                                        | 2.0                      | 2.33          |
| Ca      | 0.07                                  | 0.32                                                       | 0.36  | 0.00                                  | 0.09                                                                         | N/A                      | 8.24          |
| Mn      | 0.05                                  | 0.28                                                       | 0.28  | 0.15                                  | 0.03                                                                         | 79.3                     | 11.93         |
| Ga      | 0.00                                  | 0.00                                                       | 1.00  | 0.00                                  | 0.00                                                                         | N/A                      | 0.00          |
| P       | 0.05                                  | 0.19                                                       | 0.44  | 0.07                                  | 0.14                                                                         | 88.6                     | 11.28         |
| Zn      | 0.01                                  | 0.00                                                       | 10.81 | 0.00                                  | 0.00                                                                         | N/A                      | 0.00          |
| Zr      | 0.08                                  | 0.14                                                       | 0.97  | 0.00                                  | 0.08                                                                         | N/A                      | 8.73          |
| Cr      | 0.00                                  | 0.01                                                       | 0.84  | 0.00                                  | 0.01                                                                         | N/A                      | 8.98          |
| K       | 0.05                                  | 0.32                                                       | 0.27  | 0.06                                  | 0.05                                                                         | 23.6                     | 9.17          |
| S       | 0.23                                  | 0.30                                                       | 1.31  | 0.21                                  | 0.36                                                                         | 73.3                     | 6.45          |
| V       | 0.01                                  | 0.03                                                       | 0.51  | 0.00                                  | 0.03                                                                         | N/A                      | 8.55          |
| Mg      | 0.06                                  | 0.00                                                       | 1.00  | 0.00                                  | 0.03                                                                         | N/A                      | 12.06         |
| O       | 61.54                                 | 19.80                                                      | 5.31  | 61.46                                 | 60.04                                                                        | 2.3                      | 7.84          |





**Fig. 6.** Algorithm of autonomous analysis of spectrum by LASMA-LR. CH1 and CH2 are the two registration channels of ADC. Tres. is resolution used for spectrum analysis. Tmax. is time limit for spectrum analysis. 0.1 and 0.9 are the levels of the channels' dynamic ranges. Mean (CH1) and mean (CH2) are the mean intensities calculated for the last 10  $\mu$ s.

landing. The sequence of loading the lunar regolith samples into the instrument will be specified based on the spacecraft and its manipulator operation programs. The pass of the instrument to the operating mode, in which the samples are analyzed, occurs by an external control command. Based on the data on the analysis accuracy dependence on the number of spectra analyzed (Fig. S1), it is assumed that the duration of the analysis cycle for one sample will be about 4 h [50]. Since the sample receiving unit of the LASMA-LR instrument is designed for loading 11 regolith samples, then to analyze all samples it will be necessary to perform 11 independent switches on. After that the repetitive analyses can be carried out, which will allow accumulating more data allowing for better statistics on the regolith composition.

An important advantage of the LASMA-LR instrument is its

ability to perform measurements autonomously and with a minimal set of control commands. After power is applied to the instrument, a certain number of control commands are transmitted to set it in operating mode. Then, the device performs the measurement program automatically and saves the data in the internal memory, until the data acquisition is stopped by command and the instrument is turned off. During operation, the instrument automatically adjusts the parameters required to perform the measurements. Thus, in fact, operator control is required only when the instrument is turned on (to set the desired operating mode) and when it is turned off (to return to standby mode and/or transmit the saved scientific data). The rest of the time the instrument carries out long-term mass spectrometric measurements autonomously (Fig. S3).

The main operating mode of the LASMA-LR instrument is the analysis of the element and isotope composition of the regolith by the LIMS method. This mode is implemented by one external command according to the following algorithm. After receiving the command to start the analysis, the basic parameters used in this analysis session are set to zero, and two calibration spectra are recorded, indicating the service ability of the measuring path. Then, in accordance with the parameters of the start measurements command, the codes of digital-to-analog converters are set to supply the required initial high voltages to the detector and to the attenuator. The operating cycle of the laser emitter is started, and the spectrum obtained as a result of this cycle is analyzed by the processor to determine its quality and to select the instrument's further actions to obtain optimal mass spectra (Fig. 6). The following parameters are introduced into this algorithm and recorded for each spectrum:

- a (0/1) – presence or absence of spectral peaks in the spectrum;
- b (0/1) – absence or presence of off-scale spectral peak in the least sensitive channel;
- c (0/1) – absence or presence of broad peaks in the spectrum in the specified time range.

Parameter *a*, by the presence of peaks in the spectrum, indicates the sufficiency of the laser energy for ion formation; parameter *b* indicates a too high detector voltage leading to an off-scale in the least sensitive channel of the instrument and the impossibility of correct determining the peak integrals for quantitative analysis; parameter *c* monitors an excess of laser energy leading to increased ion production and the resulting drop in spectral resolution due to ion overload of the mass analyzer. The selection of the further actions basing on the spectrum quality is carried out using a statistical sample of the three previous spectra. So, for example, if there are no peaks in all three spectra ( $a = 1$ ), a command is issued to decrease the voltage at the attenuator corresponding to an increase in the laser energy, etc. The analysis of spectra in real time and the presence of feedback allow the adjustment of the nominal operating mode of the instrument (i.e. automatic gain control), which provides measurement in an automatic mode without any external control.

The measurement algorithm includes continuous scanning of laser radiation over the sample surface. This is primarily due to crater formation during laser ablation at one point on the sample surface, which affects the characteristics of the ion beam and, thereby, the process of spectral formation itself. It leads to instability in the obtained mass spectra. To eliminate this effect, the sample is displaced by about 50  $\mu\text{m}$  after ten laser pulses at one point and the analysis is repeated. After 45 shifts in one direction, the movement is reversed and analysis continues. Thus, the device is in fact in endless measurement cycle, which stops after receiving the power removing or stop measurement command.

The obtained mass spectra are stored in the 64 MB internal flash memory. This volume is sufficient to store 2000 spectra. If the memory is full, overwriting with the loss of the previously saved information starts. To avoid this, it is necessary to turn on the measurement mode for a time corresponding to the memory volume of the instrument. With a laser frequency of 0.1 Hz the memory filling time is 5.5 h. If for some reason it is impossible to perform a measurement cycle for less than 5.5 h or if it is impossible to clear the memory by transmitting information to the Earth, the instrument can operate in another measurement mode. In this mode the mass spectra not containing mass peaks are not stored in the flash memory. It allows effectively increase the number of useful spectra by rejecting empty spectral data. The disadvantage of this mode is the absence of data on *a*, *b*, and *c* parameters as well as

telemetry data contained in the rejected spectra. Nevertheless, this mode seems to be optimal for increasing the statistical sample of spectral data and/or decreasing the array transmitted to the Earth.

## 7. Conclusion

The laser ionization time-of-flight mass spectrometer LASMA-LR is able to analyze the elemental and isotopic composition of solid samples on the atmosphereless planetary bodies. The analysis is based on the atomization and ionization of matter by pulsed laser radiation and the measurement of the time of flight of ions from the sample to the detector, which depends on their charge and mass. The limit of detection for element analysis is at least 50 ppmA in one spectrum and 5 ppmA at analysis of 100 spectra. It is expected that the relative error of element analysis in the course of the Luna-25 and Luna-27 missions will be no more 10 % for major elements. The design of the instrument allows precise positioning of the sample and its layer-by-layer analysis to a depth of 10  $\mu\text{m}$ . The data obtained by the LASMA-LR mass spectrometer in course of the Luna-25 and Luna-27 missions can be used to solve a wide range of scientific tasks, including the classification of lunar rocks and minerals, the analysis of the lunar dust composition, the search of rare earth elements, etc. Achievement of these tasks will contribute to the study of fundamental issues related to the conditions of the Moon formation and its evolution. Moreover, the LASMA-LR measurements will be applicable to the solution of a number of applied problems of the Moon exploration.

With the LASMA-LR instrument we have demonstrated that it is possible to provide all these analytical capabilities in a very compact instrument, lightweight (<3 kg) and at low power (<10 W), which lends itself to operational concepts not only for robotic probes landed on the Moon, but also for proposed human spaceflight missions to the Moon and robotic missions to asteroids for the local prospection of mineral resources with a portable device.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

The authors are deeply grateful to B.T. Karimov (SKB KP IKI RAS) for the constructive implementation of the instrument as a whole. PW, DL, and JJ are grateful to the financial support by the Swiss National Science Foundation and the PRODEX programme of ESA.

## Author statement

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at

<https://doi.org/10.1016/j.ijms.2021.116676>.

## References

- G.G. Managadze, P. Wurz, R.Z. Sagdeev, A.E. Chumikov, M. Tulej, M. Yakovleva, N.G. Managadze, A.L. Bondarenko, Study of the main geochemical characteristics of Phobos' regolith using laser time-of-flight mass spectrometry, *Sol. Syst. Res.* 44 (2010) 376–384, <https://doi.org/10.1134/S0038094610050047>.
- G.G. Managadze, A.A. Safronova, K.A. Luchnikov, E.A. Vorobyova, N.S. Duxbury, P. Wurz, N.G. Managadze, A.E. Chumikov, R.K. Khamizov, A new method and mass-spectrometric instrument for extraterrestrial microbial life detection using the elemental composition analyses of Martian regolith and permafrost/ice, *Astrobiology* 17 (5) (2017) 448–458, <https://doi.org/10.1089/ast.2016.1511>.
- A. Riedo, A. Bieler, M. Neuland, M. Tulej, P. Wurz, Performance evaluation of a miniature laser ablation time-of-flight mass spectrometer designed for in situ investigations in planetary space research, *J. Mass Spectrom.* 48 (1) (2013a) 1–15, <https://doi.org/10.1002/jms.3157>.
- M. Tulej, A. Riedo, M. Iakovleva, P. Wurz, On applicability of a miniaturised laser ablation time of flight mass spectrometer for trace elements measurements, *Int. J. Spectrosc.* (2012), <https://doi.org/10.1155/2012/234949>. Article ID 234949.
- P. Wurz, M. Tulej, A. Riedo, V. Grimaudo, R. Lukmanov, N. Thomas, Investigation of the surface composition by laser ablation/ionisation mass spectrometry, *Lunar Surface Science Workshop* (2020). LPI Contribution No. 2241, id.5061.
- R.Z. Sagdeev, A.V. Zakharov, Brief history of the Phobos mission, *Nature* 341 (6243) (1989) 581–585, <https://doi.org/10.1038/341581a0>.
- R. Pellinen, J. Piironen, J. Silén, R.Z. Sagdeev, G.G. Managadze, I. Shutyaev, P. Timofeev, A. Bondarenko, V. Ter-Mikaelian, Laser-ionization studies with the technical models of the LIMA-D/PHOBOS experiment, *Adv. Space Res.* 10 (3–4) (1990) 57–61, [https://doi.org/10.1016/0273-1177\(90\)90326-U](https://doi.org/10.1016/0273-1177(90)90326-U).
- X. Li, W.B. Brinckerhoff, G.G. Managadze, D.E. Pugel, C.M. Corrigan, J.H. Doty, Laser ablation mass spectrometer (LAMS) as a standoff analyzer in space missions for airless bodies, *Int. J. Mass Spectrom.* 323 (2012) 63–67, <https://doi.org/10.1016/j.ijms.2012.06.020>.
- A. Riedo, C. de Koning, A.H. Stevens, A. McDonald, A. Cedeño López, M. Tulej, P. Wurz, P. Ehrenfreund, The detection of microbes in Martian mudstone analogues using laser ablation ionization mass spectrometry at high spatial resolution, *Astrobiology* 20 (10) (2020) 1224–1235, <https://doi.org/10.1089/ast.2019.2087>.
- G.G. Managadze, I. Shutyaev, Exotic instruments and applications of laser ionization mass spectrometry in space research, in: A. Vertes, R. Gijbels, F. Adams (Eds.), *Laser Ionization Mass Analysis*, Wiley, New York, 1993, pp. 505–547.
- E.M. Galimov, Phobos sample return mission: scientific substantiation, *Sol. Syst. Res.* 44 (1) (2010) 5–14, <https://doi.org/10.1134/S0038094610010028>.
- L.M. Zelenyi, A.V. Zakharov, Phobos-Grunt project: devices for scientific studies, *Sol. Syst. Res.* 44 (5) (2010) 359–361, <https://doi.org/10.1134/S0038094610050011>.
- I.G. Mitrofanov, L.M. Zelenyi, V.I. Tret'yakov, V.P. Dolgoplov, Science program of lunar landers of "Luna-Glob" and "Luna-Resource" missions, *Lunar and Planetary Science Conference* 42 (2011) 1798.
- A. Calzada-Díaz, K.H. Joy, I.A. Crawford, S. Strelkopytov, The petrology, geochemistry, and age of lunar regolith breccias Miller Range 090036 and 090070: insights into the crustal history of the Moon, *Meteoritics Planet. Sci.* 52 (1) (2017) 3–23, <https://doi.org/10.1111/maps.12737>.
- L. Haskin, P. Warren, Lunar chemistry, in: G. Heiken, D. Vaniman, B.M. French (Eds.), *The Lunar Sourcebook: A User's Guide to the Moon*, Lunar and Planetary Institute and Cambridge University Press, 1991, pp. 357–474.
- Z.C. Ling, A. Wang, B.L. Jolliffe, Mineralogy and geochemistry of four lunar soils by laser-Raman study, *Icarus* 211 (1) (2011) 101–113, <https://doi.org/10.1016/j.icarus.2010.08.020>.
- M.B. Neuland, S. Meyer, K. Mezger, A. Riedo, M. Tulej, P. Wurz, Probing the Allende meteorite with a miniature laser-ablation mass analyser for space application, *Planet. Space Sci.* 101 (2014) 196–209, <https://doi.org/10.1016/j.pss.2014.03.009>.
- M.B. Neuland, V. Grimaudo, K. Mezger, P. Moreno-García, A. Riedo, M. Tulej, P. Wurz, Quantitative measurement of the chemical composition of geological standards with a miniature laser ablation/ionization mass spectrometer designed for in situ application in space research, *Meas. Sci. Technol.* 27 (3) (2016), <https://doi.org/10.1088/0957-0233/27/3/035904>, 035904.
- D.S. McKay, D.W. Ming, Properties of lunar regolith, *Developments in Soil Science* vol. 19 (1990) 449–462, [https://doi.org/10.1016/S0166-2481\(08\)70360-X](https://doi.org/10.1016/S0166-2481(08)70360-X).
- P. Wurz, D. Abplanalp, M. Tulej, H.A. Lammer, Neutral gas mass spectrometer for the investigation of lunar volatiles, *Planet. Space Sci.* 74 (2012) 264–269, <https://doi.org/10.1016/j.pss.2012.05.016>.
- D. Heather, E. Sefton-Nash, The ESA prospect payload for Luna 27: development status, in: *EGU General Assembly Conference Abstracts*, 2020, p. 22244.
- K.L. Donaldson Hanna, D.J.P. Martin, K.H. Joy, J.D. Carpenter, N.E. Bowles, PROSPECT user group characterization of lunar highlands regolith simulants in preparation for drilling and sampling into the polar regolith by ESA's PROSPECT package, *Proc. Lunar Planet. Sci. Conf.* (2017) 48.
- R. Ganapathy, E. Anders, Bulk compositions of the moon and earth, estimated from meteorites, *Lunar and Planetary Science Conference Proceedings* 5 (1974) 1181–1206.
- E. Hand, Lunar impact tosses up water and stranger stuff, *Nature* (2009), <https://doi.org/10.1038/news.2009.1087>.
- G.R. Gladstone, D.M. Hurley, K.D. Retherford, P.D. Feldman, W.R. Pryor, J.Y. Chaufray, M. Versteeg, T.K. Greathouse, A.J. Steffl, H. Throop, J.Wm Parker, D.E. Kaufmann, A.F. Egan, M.W. Davis, D.C. Slater, J. Mukherjee, P.F. Miles, A.R. Hendrix, A. Colaprete, S.A. Stern, LRO-LAMP observations of the LCROSS impact plume, *Science* 330 (6003) (2010) 472–476, <https://doi.org/10.1126/science.1186474>.
- M.V. Djachkova, M.L. Litvak, I.G. Mitrofanov, A.B. Sanin, Selection of luna-25 landing sites in the South polar region of the moon, *Sol. Syst. Res.* 51 (3) (2017) 185–195, <https://doi.org/10.1134/S0038094617030029>.
- R. Tartèse, M. Anand, J. Gattaceca, K.H. Joy, J.I. Mortimer, J.F. Pernet-Fisher, S. Russell, J.F. Snape, B.P. Weiss, Constraining the evolutionary history of the Moon and the inner Solar System: a case for new returned Lunar samples, *Space Sci. Rev.* 215 (8) (2019) 54, <https://doi.org/10.1007/s11214-019-0622-x>.
- S.G. Pugacheva, V.V. Shevchenko, The chemical composition of regolith at the Moon's South Pole, according to data of Lunar Prospector and Lunar Reconnaissance Orbiter missions, *Lunar and Planetary Science Conference* 41 (2010) 1297.
- Z. Wang, Y. Wu, D.T. Blewett, E.A. Cloutis, Y. Zheng, J. Chen, Submicroscopic metallic iron in lunar soils estimated from the in situ spectra of the Chang'E-3 mission, *Geophys. Res. Lett.* 44 (8) (2017) 3485–3492, <https://doi.org/10.1002/2017GL072652>.
- M. Anand, R. Tartèse, J.J. Barnes, Understanding the origin and evolution of water in the Moon through lunar sample studies, *Phil. Trans. Math. Phys. Eng. Sci.* 372 (2024) (2014) 20130254, <https://doi.org/10.1098/rsta.2013.0254>.
- S. Li, P.G. Lucey, R.E. Milliken, P.O. Hayne, E. Fisher, J.P. Williams, D.M. Hurley, R.C. Elphic, Direct evidence of surface exposed water ice in the lunar polar regions, *Proc. Natl. Acad. Sci. Unit. States Am.* 115 (36) (2018) 8907–8912, <https://doi.org/10.1073/pnas.1802345115>.
- M. Anand, L.A. Taylor, M.A. Nazarov, J. Shu, H.K. Mao, R.J. Hemley, Space weathering on airless planetary bodies: clues from the lunar mineral haptite, *Proc. Natl. Acad. Sci. Unit. States Am.* 101 (18) (2004) 6847–6851, <https://doi.org/10.1073/pnas.0401565101>.
- O.A. Bogatkov, A.I. Gorshkov, A.V. Mokhov, N.A. Ashikhmina, L.O. Magazina, The first finding of native molybdenum, silver sulfide, and iron-tin alloy in the lunar regolith, *Geochem. Int.* 39 (6) (2001) 604–608.
- A.V. Mokhov, T.A. Gornostaeva, P.M. Kartashov, A.P. Rybchuk, O.A. Bogatkov, Native alloys of the Pd–Pt and Ni–Cu–Al systems from the AS Luna-24, *Dokl. Earth Sci.* 481 (1) (2018) 898–901, <https://doi.org/10.1134/S1028334X18070103>.
- A.V. Mokhov, P.M. Kartashov, A.P. Rybchuk, T.A. Gornostaeva, O.A. Bogatkov, Tantalum–niobate from the Apollo-17 regolith, *Dokl. Earth Sci.* 478 (1) (2018) 112–114, <https://doi.org/10.1134/S1028334X18010245>.
- K.J. Kim, A research trend on Lunar resources and Lunar base, *The Journal of The Petrological Society of Korea* 26 (4) (2017) 373–384, <https://doi.org/10.7854/JPSK.2017.26.4.373>.
- A.T. Basilevsky, S.S. Krasilnikov, M.A. Ivanov, M.I. Malenkov, G.G. Michael, T. Liu, J.W. Head, D.R. Scott, L. Lark, Potential lunar base on Mons Malapert: topographic, geologic and traffic ability considerations, *Sol. Syst. Res.* 53 (5) (2019) 383–398, <https://doi.org/10.1134/S0038094619050022>.
- N. Gerdes, L.G. Fokken, S. Linke, S. Kaierle, O. Suttman, J. Hermsdorf, E. Stoll, C. Trentlage, Selective Laser Melting for processing of regolith in support of a lunar base, *J. Laser Appl.* 30 (3) (2018), <https://doi.org/10.2351/1.5018576>, 032018.
- R. Bonneville, A truly international lunar base as the next logical step for human spaceflight, *Adv. Space Res.* 61 (12) (2018) 2983–2988, <https://doi.org/10.1016/j.asr.2018.03.035>.
- C.L. McLeod, M. Krekeler, Sources of extraterrestrial rare earth elements: to the moon and beyond, *Resources* 6 (3) (2017) 40, <https://doi.org/10.3390/resources6030040>.
- G.W. Wamelink, J.Y. Frissel, W.H. Krijnen, M.R. Verwoert, P.W. Goedhart, Can plants grow on Mars and the moon: a growth experiment on Mars and moon soil simulants, *PLoS One* 9 (8) (2014), e103138, <https://doi.org/10.1371/journal.pone.0103138>.
- G.W.W. Wamelink, J.Y. Frissel, W.H.J. Krijnen, M.R. Verwoert, Crop growth and viability of seeds on Mars and Moon soil simulants, *Open Agriculture* 4 (1) (2019) 509–516, <https://doi.org/10.1515/opag-2019-0051>.
- Y. Liu, L.A. Taylor, Lunar dust: chemistry and physical properties and implications for toxicity, *NLSI Lunar Science Conference* 1415 (2008) 2072.
- C.W. Lam, R.R. Scully, Y. Zhang, R.A. Renne, R.L. Hunter, R.A. McCluskey, B.T. Chen, V. Castranova, K.E. Driscoll, D.E. Gardner, R.O. McClellan, B.L. Cooper, D.S. McKay, L. Marshall, J.T. James, Toxicity of lunar dust assessed in inhalation-exposed rats, *Inhal. Toxicol.* 25 (12) (2013) 661–678, <https://doi.org/10.3109/08958378.2013.833660>.
- L.M. Zelenyi, S.I. Popel, A.V. Zakharov, Dusty plasma at the moon. Challenges of modeling and measurements, *Plasma Phys. Rep.* 46 (2020) 527–540, <https://doi.org/10.1134/S1063780X20050104>.
- Managadze G.G., Managadze N.G. TOF Mass Spectrometer. Patent 2096861 (RF). Priority of Invention: 1994. Registered: 1997. Published in Russian Bulletin of Inventions No. 32.



- [47] A. Cedeño López, V. Grimaudo, A. Riedo, M. Tulej, R. Wiesendanger, R. Lukmanov, P. Moreno-García, E. Lörtscher, P. Wurz, P. Broekmann, Characterization of femtosecond laser ablation processes on as-deposited SnAg solder alloy using laser ablation ionization mass spectrometry, *Spectrochim. Acta B Atom. Spectrosc.* 180 (2021) 106145, <https://doi.org/10.1016/j.sab.2021.106145>.
- [48] R. Lukmanov, M. Tulej, R. Wiesendanger, A. Riedo, V. Grimaudo, N. Ligterink, C. de Koning, A. Neubeck, D. Wacey, P. Wurz, Multi-wavelength ablation/ionisation and mass spectrometric analysis of 1.88 Ga Gunflint Chert, *Astrobiology* (2021) (submitted for publication).
- [49] S. Shuttleworth, Optimisation of laser wavelength in the ablation sampling of glass materials, *Appl. Surf. Sci.* 96 (1996) 513–517, [https://doi.org/10.1016/0169-4332\(95\)00505-6](https://doi.org/10.1016/0169-4332(95)00505-6).
- [50] A.E. Chumikov, V.S. Cheptsov, N.G. Managadze, Accuracy of analysis of the elemental and isotopic composition of regolith by laser time-of-flight mass spectrometry in the future Luna-Glob and Luna-Resurs-1 missions, *Sol. Syst. Res.* 54 (4) (2020) 288–294, <https://doi.org/10.1134/S0038094620030028>.
- [51] A. Riedo, S. Meyer, B. Heredia, M.B. Neuland, A. Bieler, M. Tulej, I. Leya, M. Iakovleva, K. Mezger, P. Wurz, Highly accurate isotope composition measurements by a miniature laser ablation mass spectrometer designed for in situ investigations on planetary surfaces, *Planet. Space Sci.* 87 (2013b) 1–13, <https://doi.org/10.1016/j.pss.2013.09.007>.
- [52] A. Riedo, M. Neuland, S. Meyer, M. Tulej, P. Wurz, Coupling of LMS with a fs-laser ablation ion source: elemental and isotope composition measurements, *J. Anal. Atomic Spectrom.* 28 (8) (2013c) 1256–1269, <https://doi.org/10.1039/C3JA50117E>.
- [53] G.I. Ramendik, O.I. Kryuchkova, D.A. Tyurin, T.R. McHedlidze, M.S. Kaviladze, Factors affecting the relative sensitivity coefficients in spark and laser plasma source mass spectrometry, *Int. J. Mass Spectrom. Ion Process.* 63 (1985) 1–15, [https://doi.org/10.1016/0168-1176\(85\)87036-1](https://doi.org/10.1016/0168-1176(85)87036-1).
- [54] R. Wiesendanger, M. Tulej, A. Riedo, S. Frey, H. Shea, P. Wurz, Improved detection sensitivity for heavy trace elements using a miniature laser ablation ionisation mass spectrometer, *J. Anal. Atomic Spectrom.* 32 (2017) 2182–2188, <https://doi.org/10.1039/C7JA00193B>.