# 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

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Abstract—Laser ionization mass spectrometry is one of the most promising methods for analysis of the elemental and isotopic composition of solids in space experiments: the required instruments are highly reliable and easy to operate, no sample preparation is needed, and the spatial resolution of this method is relatively high. In view of this, the LASMA-LR laser ionization mass spectrometer was included into the list of instruments for the future Luna-Glob (*Luna-25*) and Luna-Resurs-1 (*Luna-27*) missions, where it will be used to examine the elemental and isotopic composition of lunar regolith at the landing sites. The accuracy of LASMA-LR measurements depends to a considerable extent on the size of the statistical sample of the spectral dataset. This defines the temporal parameters of operation of the mass spectrometer in a space experiment. A series of spectra of enstatite (mineral found in lunar regolith) was measured, and the instrumental accuracy of measurements with spectral datasets of different sizes was estimated. It was demonstrated that an elemental analysis accuracy of 10% is achieved by processing a set of 300 spectra, which corresponds to ~4 h of continuous LASMA-LR operation. A measurement accuracy of 1% for isotopic distributions is achieved within the same 4-hour period only for isotopes with ratios no higher than 10 : 1, while the same accuracy for isotopes with higher ratios requires an unfeasibly long analysis time.

*Keywords:* laser ionization mass spectrometry, LASMA, Luna-Glob, Luna-Resurs-1, elemental analysis, isotopic analysis

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# INTRODUCTION

Studies of the molecular, elemental, and isotopic composition of regolith and dust are integral to virtually all lander missions. These studies help clarify the processes of evolution of astronomical bodies, determine their physical and chemical characteristics, evaluate the prospects for their colonization, and solve other fundamental and applied problems of various kinds. Laser ionization mass spectrometry (LIMS) is one of the most promising methods for analysis of the elemental and isotopic composition of solids in space experiments: the required instruments are highly reliable and easy to operate, no sample preparation is needed, and the spatial resolution of this method is relatively high (Tulej et al., 2012, 2015; Riedo et al., 2013a). LIMS for space applications has been developing rapidly in the recent decades, and a number of prototypes and flight instruments have already been constructed (Tulej et al., 2015; Managadze et al., 2010; 2017). One of them, LASMA, was installed aboard the Fobos-Grunt space probe, and its modification LASMA-LR is included into the list of instruments for the future Luna-Glob (*Luna-25*) and Luna-Resurs-1 (*Luna-27*) missions (Managadze et al., 2010; Mitrofanov et al., 2011).

The elemental and isotopic composition of regolith is analyzed by LASMA-LR in the following way: a sample is mounted on a rotating disk at a distance corresponding to the focal distance of the laser unit and is then irradiated by a 7-ns-long pulse produced by the Nd:YAG laser with a wavelength of 1.064  $\mu$ m. The irradiating power density is ~10<sup>9</sup> W/cm<sup>2</sup> (Fig. 1). This results in complete atomization and ionization of the sample, and severe overheating leads to ejection of the produced ions in the form of a plasma plume.

High-velocity ions emitted from the freely spreading plasma enter the time-of-flight mass analyzer and are separated according to the time of flight as per the following formula:

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

where T is the time within which ions with energy E and mass M traverse field-free distance L. Time-separated ions are reflected in the decelerating field of the

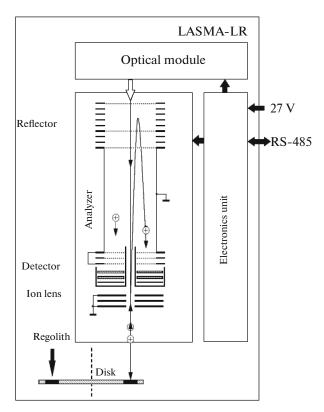


Fig. 1. Functional diagram of the LASMA-LR instrument.

electrostatic reflector and are detected by the secondary-electron multiplier. The signal is then fed to a high-speed analog-to-digital converter and stored in memory in the form of a separate spectrum. The timeof-flight of ions and the signal intensity allow one to determine accurately the mass of ions and their relative concentrations. The distribution and amplitude of isotopes provide an opportunity to indentify chemical elements; analyzing the intensity of mass peaks of elements, one may then determine the chemical (elemental and isotopic) composition of the studied substance (Managadze et al., 2010, 2017).

It is important that the accuracy of LASMA-LR measurements depends to a considerable extent on the size of the statistical sample of the spectral dataset. The spectra acquisition time depends on the size of the statistical sample needed to reach the given accuracy, and this time, in turn, defines the temporal parameters of LASMA-LR operation in a space experiment. In view of this, the present study was aimed at examining the dependence of the accuracy of determination of the elemental and isotopic composition on the size of the statistical sample of the spectral dataset of the LASMA-LR flight instrument and finding the number of spectra needed to reach an accuracy of 10 and 1% of determination of the elemental and isotopic composition, respectively. This accuracy is sufficient for a wide range of tasks in planetology, geochronology, and astrobiology: preliminary analysis and selection of samples to be transported back to Earth, classification of astronomical bodies, examination of the processes of their formation and erosion of their surface, determination of the age of rocks, searching for rare-earth elements, etc. (Brinckerhoff, 2005).

#### MATERIALS AND METHODS

The object under study is enstatite, which is a mineral of the group of pyroxenes that are abundant in lunar regolith and meteorites (Reid et al., 1973; Rubin, 1997). An enstatite sample from Norway was provided by the Natural History Museum in Berlin, where its chemical composition was studied by energy-dispersive X-ray spectroscopy (EDXS) with a JEOL 8500-F field-emission scanning electron microscope (JEOL Inc., United States). The sample contained  $Al_2O_3$ , Na<sub>2</sub>O, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, MnO, CaO, and FeO oxides in the following concentrations: 0.09, 0.02, 0.04, 0.01, 57.15, 32.54, 0.04, 0.29, and 9.91 wt %, respectively. Therefore, the abundance of Al, Na, Ti, Cr, Si, Mg, Mn, Ca, Fe, and O was 0.037, 0.014, 0.105, 0.003, 19.93, 17.03, 0.012, 0.108, 2.88, and 59.98 at %, respectively. The results of microscopic studies revealed that the sample is homogeneous. This makes it certain that the instrumental analysis accuracy determined below is not affected by the target inhomogeneity.

The accuracy parameters of elemental and isotopic analysis were examined using the LASMA flight unit of the Fobos-Grunt project (Managadze et al., 2010). Its analytical part is exactly the same as that of LASMA-LR. The instrument was introduced into a vacuum chamber and evacuated to a working pressure of 5  $\times$  10<sup>-6</sup> Torr. A series of 135 enstatite spectra was then measured in the normal operating mode. The rate of spectra acquisition (0.1 Hz) was defined by the laser operation frequency. A low-frequency laser was used, since its average energy consumption is low, it does not require active cooling in a space experiment, and the technology of fabrication of such lasers for severe operating conditions is well-proven. The laser spot was  $\sim 30 \,\mu\text{m}$  in diameter. The depth of the formed crater depends on the target material and was on the order of  $10^{-7}$  m.

Specialized software for processing series of spectra and determining the percentage elemental and isotopic composition of the sample was developed in GNU Octave 3.4.3. The algorithm of its operation was as follows: spectrum stitching based on the most sensitive channel; subtraction of the baseline; determination of integrals of peaks of a separate spectrum using the method of trapezoids; normalization (reduction of integrals of peaks to their percentage distribution); averaging of the obtained abundances of elements and isotopes (in at %) and calculation of standard errors of the mean.

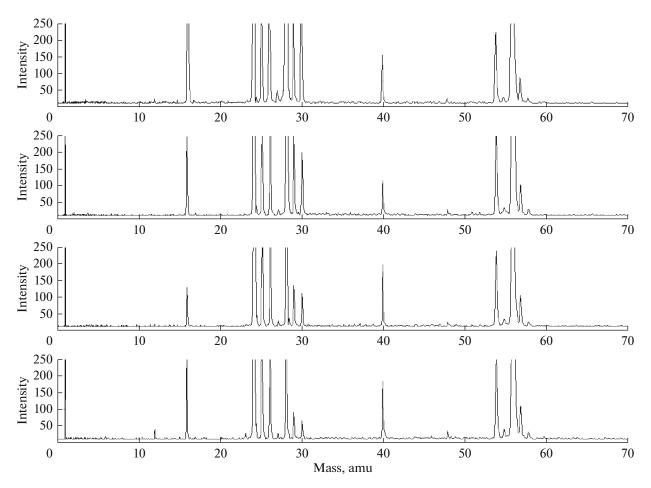


Fig. 2. Spectra of the enstatite sample, which were measured in the most sensitive channel and demonstrate reproducibility of measurements.

It is important to note that the accuracy of measurement of a certain quantity is defined by both random and systematic errors (the influence of rough errors was neglected). In LASMA measurements, the random error is defined by the relative spread of integrals of spectral peaks of elements in different spectra (Fig. 2), while the systematic error manifests itself as a permanently overstated (or understated) value of the peak integral of a certain element. For example, it follows from Fig. 2 that the value of the oxygen peak integral is significantly lower than the one corresponding to the above EDXS data on the sample composition. The influence of the systematic error on the accuracy of analysis of the elemental and isotopic composition of lunar regolith will be offset by constant coefficients (relative sensitivity coefficients, RSCs) introduced at the stage of processing of data collected in a space experiment and in the process of experimental analysis of terrestrial rocks and soils close in their composition to lunar regolith. Since these coefficients are planned to be introduced at the data processing stage and are not related in any way to the statistical accumulation of measurement results in a space experiment, all RSCs are assumed to be equal to one in the present study, and the influence of only the random error component on the measurement accuracy is considered.

## **RESULTS AND DISCUSSION**

The results of analysis of the elemental composition of enstatite obtained by processing spectra samples of different sizes are presented in Table 1. It can be seen that the accuracy of determination of the element concentration is related both to the integral of the peak of an element (i.e., its concentration) in the spectrum and, predictably, to the size of the analyzed sample. A similar effect of reduction in the accuracy of concentration measurements for less abundant elements has been observed earlier for several other laser ionization mass spectrometers (Riedo et al., 2013b, 2013c).

The large statistical spread of elements with low concentrations is attributable to their inhomogeneous distribution in the sample. Evidently, a similar pattern would also be observed for peaks of matrix elements in a strongly heterogeneous sample. Thus, it is highly likely that the instrumental (independent of the char-

Element	Sample size: 20 spectra		Sample size: 40 spectra		Sample size: 80 spectra		Sample size: 135 spectra	
	$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %	$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %	$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %	$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %
Si	$42.17\pm3.95$	9.3	$44.09\pm2.76$	6.3	$43.02 \pm 1.87$	4.3	$42.40 \pm 1.44$	3.4
Mg	$26.42 \pm 1.66$	6.3	$25.36\pm0.97$	3.8	$26.50\pm0.87$	3.3	$26.99\pm0.68$	2.5
Fe	$23.30\pm3.27$	14.0	$23.47\pm2.44$	10.4	$23.27 \pm 1.70$	7.3	$23.85 \pm 1.30$	5.5
0	$6.13\pm2.31$	37.6	$5.39 \pm 1.42$	26.4	$5.66 \pm 1.13$	20.0	$5.23\pm0.76$	14.6
Ca	$0.97\pm0.19$	20.3	$0.86\pm0.11$	12.9	$0.83\pm0.07$	8.3	$0.80\pm0.05$	6.3
Ti	$0.26\pm0.10$	38.4	$0.26\pm0.05$	21.0	$0.25\pm0.03$	12.7	$0.28\pm0.03$	10.4
Al	$0.42\pm0.25$	58.5	$0.29\pm0.12$	43.0	$0.22\pm0.063$	28.3	$0.20\pm0.038$	18.3
Mn	$0.11\pm0.02$	19.5	$0.11\pm0.014$	13.0	$0.10\pm0.01$	8.8	$0.11\pm0.008$	7.0
Na	$0.15\pm0.05$	34.5	$0.11\pm0.02$	24.7	$0.09\pm0.015$	16.8	$0.08\pm0.01$	12.5
Cr	$0.02\pm0.01$	44.0	$0.02\pm0.006$	25.2	$0.02\pm0.004$	18.2	$0.02\pm0.003$	15.3

Table 1. Results of determination of the elemental composition of enstatite with spectral datasets of different sizes

acteristics of the studied sample) analysis accuracy is defined in the present case by peaks of matrix elements (Mg, Si, Fe), while impurity elements such as Na, Al, Cr characterize the accuracy reduction due to inhomogeneity. The sole exception is oxygen: although its concentration in the sample is considerable, the standard error of the mean for it is comparable to that of impurities. Evidently, this spread of results of individual measurements is not associated with nonuniformity of the oxygen distribution in the sample, since the sample itself is a mixture of oxides; instead, it is caused by physical processes of oxygen spectrum formation such as the shift of the energy distribution maximum from the working area of the analyzer. proximity of the threshold ionization energy to the used laser radiation intensity, etc. In general, this effect is common to LIMS and is observed for all elements with their atomic masses below that of oxygen (H, C, N, etc.) (Tulej et al., 2012, 2015; Wurz et al., 2012).

Let us divide the elements in Table 1 into two groups: uniformly distributed matrix elements (Mg, Si, and Fe), which characterize the instrumental analysis accuracy, and the group containing impurity elements and oxygen. Since it is unknown how uniform the distribution of chemical elements in lunar regolith at the landing sites of Luna-Glob and Luna-Resurs-1 is, we assume that the statistical distributions of matrix elements in lunar regolith are close to those of impurities in enstatite. Thus, the first group of elements defines the minimum number of spectra needed to achieve the set analysis accuracy for an ideal target, and the second group models the accuracy for a heterogeneous sample.

According to the dependences of the relative standard error of the mean on the number of analyzed spectra, a relative instrumental accuracy of 10% for the first group of elements was achieved by processing 50 spectra; if 135 spectra were analyzed, the accuracy was no worse than 6% (Fig. 3a). Power-law extrapolation of the obtained dependences to larger statistical samples revealed that an analysis accuracy of 10% for elements of the second group (except for Al) was achieved with a set of 300 spectra (Fig. 3b). The relative standard deviation for Al was 12%. The corresponding accuracy of analysis for elements of the first group increased to 4%. A set of 400 spectra was needed to achieve an accuracy of Al identification of 10%. Thus, the data suggest that a dataset of  $\sim 300$  separate spectra will be needed to perform elemental analysis of lunar regolith with an accuracy of 10%. Since up to 80% of spectra measured for a complex sample (e.g., regolith) are discarded, a total of ~1500 spectra will be required to obtain 300 useful ones. Since the measurement time for a single spectrum is 10 s, ~4.2 h of LASMA-LR operation will be needed to accumulate 1500 spectra. In view of this, the nominal time of elemental analysis of a single target will be  $\sim 4$  h.

It should be noted that the concentrations of elements determined using LASMA-LR (Table 1) differ considerably from the EDXS values. This is attributable to the influence of the systematic error on the accuracy of mass-spectrometric analysis. As was noted above, this influence will be offset by RSCs introduced at later stages.

The accuracy of isotopic analysis was estimated based on the same spectral data. Since elements of the second group have low concentrations (the concentrations of all isotopes except the main one are at the noise level) or are monoisotopic, isotopic distributions were determined for elements of the first group. This is also warranted by the fact that isotopic ratios are independent of the sample homogeneity, i.e., the obtained statistical estimates will remain valid for any reliably identified element.

In certain cases, the measured mean isotopic concentrations differed significantly from the natural concentration (Table 2). This implies that correction coefficients (isotopic RSCs) will be needed in measurements of isotopic ratios. The large spread of data on

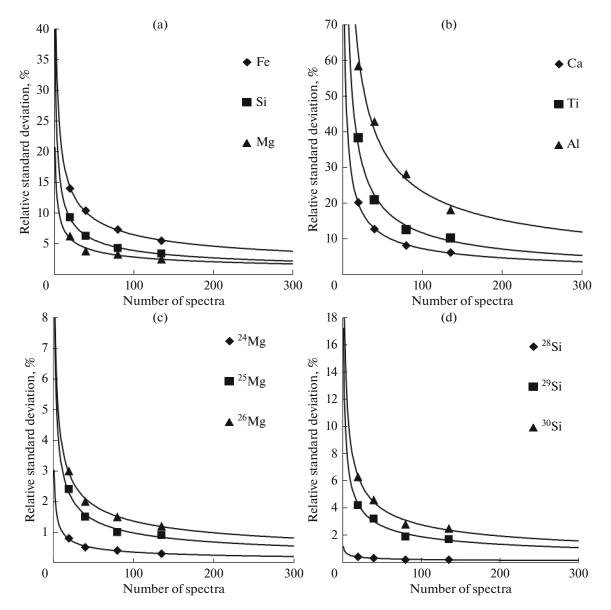


Fig. 3. Experimental dependences of the relative standard error of the mean concentration of different elements and isotopes on the number of analyzed spectra.

iron isotope <sup>58</sup>Fe and the considerable deviation of the obtained value from the natural abundance are attributable to the low concentration of this isotope and its atomic-mass overlap with <sup>58</sup>Ni. According to the measurement results, the accuracy of determination of the concentration of a certain isotope depends directly on its abundance. The same dependence was noted above in elemental analysis. In view of this, the data for isotopic distributions of matrix elements containing commeasurable amounts of several nuclides should be the most accurace; as isotopic ratios increase, the accuracy of their measurement decreases.

Specifically, an accuracy of 1% for all magnesium isotopes was achieved by processing 200 spectra (Fig. 3c), while ~600 spectra are needed to determine

all isotopic ratios of silicon with the same accuracy (Fig. 3d). Thus, with all the above time estimates for elemental analysis factored in, the set accuracy of measurement of concentrations of isotopes with a natural abundance ratio of  $\sim 8 : 1 ({}^{24}\text{Mg} : {}^{25}\text{Mg} \text{ and } {}^{24}\text{Mg} : {}^{26}\text{Mg})$  will be achieved in  $\sim 3$  h of operation, and  $\sim 9$  h will be needed for isotopes with a ratio of  $\sim 30 : 1$  (Si isotopes). The analysis time for isotopes with higher ratios is unfeasibly long. For example, a set of 2000 useful spectra ( $\sim 30$  h of operation) will be required to analyze the concentrations of isotopes with a ratio of  $\sim 50 : 1 ({}^{56}\text{Fe} : {}^{57}\text{Fe})$ , and approximately 200000 spectra ( $\sim 12$  d of continuous operation of the mass analyzer) will be needed for nuclides with a ratio of  $\sim 300 : 1 ({}^{56}\text{Fe} : {}^{58}\text{Fe})$ . Thus, isotopes with a ratio of  $\sim 10 : 1$  (or

SOLAR SYSTEM RESEARCH Vol. 54 No. 4 2020

Isotope		Sample size: 20 spectra		Sample size: 40 spectra		Sample size: 80 spectra		Sample size: 135 spectra	
		$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %	$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %	$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %	$(x \pm \sigma_x)$ , at %	<i>S</i> <sub>r</sub> , %
<sup>24</sup> Mg	78.99	$76.68\pm0.61$	0.8	$76.78\pm0.37$	0.5	$76.34\pm0.28$	0.4	$76.89 \pm 0.22$	0.3
<sup>25</sup> Mg	10.00	$10.55\pm0.25$	2.4	$10.52\pm0.16$	1.5	$10.58\pm0.10$	1.0	$10.40\pm0.09$	0.9
<sup>26</sup> Mg	11.01	$12.76\pm0.38$	3.0	$12.69\pm0.25$	2.0	$13.06\pm0.19$	1.5	$12.69\pm0.15$	1.2
<sup>28</sup> Si	92.23	$92.40\pm0.36$	0.4	$91.69\pm0.29$	0.3	$91.28\pm0.18$	0.2	$91.88\pm0.15$	0.2
<sup>29</sup> Si	4.68	$4.30\pm0.18$	4.2	$4.70\pm0.15$	3.2	$4.87\pm0.09$	1.9	$4.61\pm0.07$	1.7
<sup>30</sup> Si	3.09	$3.29\pm0.21$	6.3	$3.60\pm0.16$	4.6	$3.83\pm0.10$	2.8	$3.50\pm0.08$	2.5
<sup>54</sup> Fe	5.85	$5.78\pm0.19$	3.3	$5.67\pm0.14$	2.5	$5.61\pm0.08$	1.6	$5.59\pm0.06$	1.2
<sup>56</sup> Fe	91.75	$91.69\pm0.27$	0.3	$91.58\pm0.22$	0.2	$91.65\pm0.20$	0.2	$91.70\pm0.14$	0.1
<sup>57</sup> Fe	2.12	$1.93\pm0.11$	5.7	$2.15\pm0.09$	4.4	$2.20\pm0.07$	3.5	$2.16\pm0.05$	2.7
<sup>58</sup> Fe	0.28	$0.58\pm0.10$	17.4	$0.59\pm0.07$	12.0	$0.52\pm0.06$	12.7	$0.53\pm0.04$	8.7

**Table 2.** Isotopic distributions of elements of the first group for statistical samples of different sizes. Data on the natural abundance of isotopes were taken from (Rosman and Taylor, 1999)

lower) will be identified with an accuracy of 1% in 4 h. This analysis time seems to be optimal, since much longer times are needed for isotopes with higher ratios; in addition, this value agrees well with the nominal elemental analysis time for a single sample. Since isotopic ratios should not vary from one lunar regolith sample to another if the sampling sites were close to each other, the aggregate statistics for all samples is expected to be used in the analysis of isotopic distributions for low-abundance isotopes. The design of the LASMA sampler allows one to analyze 11 regolith samples in a space experiment (Managadze et al., 2010). Thus, a set of no less than 3300 useful spectra may be compiled. This set will make it possible to achieve an accuracy of 1% in characterizing the isotopic distributions for nuclides with natural abundance ratios of 50 : 1 and higher.

It should be noted that the random error component is affected by several factors such as the statistics of discrete events, the reproducibility of the power density of laser radiation, fluctuations of the energy distributions of elements relative to the admissible energy range of the time-of-flight mass analyzer, etc., which thus influence the accuracy of elemental and isotopic analysis. In fact, these factors are largely responsible for the difference in accuracy of elemental and isotopic analysis (see above). However, this study was not aimed at examining the individual influence of each factor on the end result. The measurements discussed above characterize the integral influence of all random factors on the accuracy of analysis performed by a specific onboard laser time-of-flight mass spectrometer and allow one to determine its nominal operating conditions in a space experiment. This was the primary goal of the study.

# CONCLUSIONS

Our experimental studies aimed at determining the size of the spectral dataset and the time of analysis of a single sample needed to achieve an accuracy of 10 and 1% of determination of the elemental and isotopic composition, respectively, revealed the following.

(1) A set of 300 spectra is sufficient to achieve the indicated accuracy of elemental analysis. This corresponds to  $\sim$ 4 h of continuous operation of the LASMA-LR instrument.

(2) The accuracy of elemental analysis and the accuracy of determination of isotopic distributions depend both on the number of observations and on the concentrations of elements and isotopes.

(3) A measurement accuracy of 1% for isotopic distributions is achieved within the same 4-h period only for isotopes with ratios no higher than 10: 1, while the same accuracy for isotopes with higher ratios requires an unfeasibly long analysis time.

(4) Assuming that the isotopic composition of different samples of lunar regolith taken at the same landing site is uniform, one may measure the isotopic distributions by analyzing spectral data from different samples simultaneously. This should help ease the restrictions related to isotope concentrations and should make it possible to characterize the isotopic distributions for nuclides with concentration ratios of 50 : 1 and above with an accuracy of 1%.

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