



A neutral gas mass spectrometer for the investigation of lunar volatiles

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ABSTRACT

We developed a compact time-of-flight mass spectrometer (TOF-MS) for the sensitive investigation of gas samples in planetary missions. The advantage of a TOF-MS for space research is its fairly simple and robust mechanical design and its moderate need for resources. Moreover, because a TOF-MS system records all masses at the same time it has high sensitivity. The performance as established by our prototype instrument is a mass resolution of about $m/\Delta m = 1100$ and a mass range of 1000 amu (in principle the mass range is only limited by the accumulation memory). A TOF-MS is a pulsed system and mass spectra are recorded with high temporal cadence, typically 10,000 spectra per second. A high dynamic range is achieved by histogramming these mass spectra for a certain period, i.e., for accumulation periods of seconds a dynamic range about 10^7 is achieved. With our prototype instrument we established a detection limit of 10^{-16} mbar (corresponding to a number density of about 1 cm^{-3}), which means that at a total pressure of 10^{-10} mbar we still have 6 decades of dynamic range. This instrument performance will allow for very sensitive measurements of the lunar exosphere, either from ground or from low-lunar orbit.

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1. Introduction

Little is known on the composition and structure of the tenuous lunar atmosphere, actually an exosphere, and it remained poorly understood more than forty years after the first Apollo landings. Species detected in the lunar exosphere are the volatile species CH_4 , N_2 , CO_2 , He, NH_3 , and Ar, and upper limits have been derived for H_2 , CO, Kr, and Xe. Their densities sum up to a total density of about $2 \times 10^5 \text{ cm}^{-3}$ (Stern, 1999), and references therein). In contrast, from the observation of the large electron content in the lunar ionosphere, which is still debated (see review by Imamura et al., 2010), one would infer the total neutral density to be at least a factor 10 higher (Stern et al., 1997). Alternatively, it has been suggested recently that the dust in the lunar exosphere might be the source of these electrons (Stubbs et al., 2011). Glenar et al. (2011) reanalysed the lunar horizon glow data observed in the Apollo 15 photographic data and produced quantitative dust altitude profiles. The authors conclude that the exospheric dust is composed of sub- μm sized dust grains with dust densities below 0.1 part/cm^3 at the surface and scale heights of about 10 km. Although the dust might have an important role in the lunar exosphere, from the instrumental point of view the actual dust densities are low and correspond to a Class 100 clean room environment.

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The reasons for the difficulty of neutral gas observations are the very low number densities of the exospheric species, and the complexity of models due to the multiplicity of mechanisms responsible for the input and loss of atomic species to and from the exosphere, which include ion induced sputtering (IS), photon stimulated desorption (PSD) and micro-meteoroid impact vaporisation (MIV) resulting in inputs to the exosphere, and photo-ionisation, surface adsorption and thermal escape resulting in losses from the lunar gravity field (e.g. Stern, 1999; Killen and Ip, 1999; Hunten and Sprague, 1997; Mendiolo et al., 1999).

The composition of noble gases in the lunar exosphere (largely inferred from studies of gas trapped in lunar regolith samples) indicates that these may be dominated by a solar wind source, but with additional contributions probably from the interior of the Moon (e.g. Hodges Jr. and Hoffman, 1975; Wieler et al., 1996). The latter idea is supported by observations of episodic outgassing of radon (Gorenstein et al., 1974a, 1974b, Hodges Jr. and Hoffman, 1975); see Lawson et al. (2005) for a review of the literature. Because the solar wind impinges on the lunar surface with energies of about 1 keV/ nucleon, H, He and other solar wind species are absorbed in the surface material (the regolith grains, rocks, etc.) and are trapped. A fraction of the noble gases is subsequently released to become part of the lunar exosphere (e.g., Hinton and Tausch, 1964; Johnson, 1971; Hodges, 1973).

The flux of heavier, more refractory, elements to the lunar exosphere is dominated by ion sputtering (Wurz et al., 2007). In this case, the lunar surface material will be the primary source reservoir for elements in the lunar exosphere such as Si, Ti, Al, Fe, Mg, Ca, and O, which have not yet been observed directly in the

neutral exosphere. However, pickup ions of refractory elements of lunar origin have been identified in the solar wind, which attest to the sputtering process operating (Kirsch et al., 1998; Mall et al., 1998). Stern (1999) reviewed upper limits for the abundances of refractory and some other elements. Based on modelling, the expected densities of these elements are often several orders of magnitude lower than these upper limits (Wurz et al., 2007).

Within the last decades, much work has focused on the neutral sodium and potassium components of the lunar exosphere as these can be studied from the Earth by telescopic observations (Potter and Morgan, 1998; Flynn and Mendillo, 1993). However, the release into the exosphere and the strong interaction with the solar photons of these two elements is special, and does not represent the exospheric distribution of other species. The densities of Na and K in the exosphere at the surface are not only the result of sputtering but also to a larger extent most likely the result of PSD (Sprague et al., 1992; Wurz et al., 2007). In addition it has been estimated that up to 15% of the observed Na in the exosphere can be attributed to the impact of micro-meteors (Flynn and Mendillo, 1993).

2. The composition of the lunar exosphere

To understand the measurement requirements to advance our understanding of the lunar exosphere the exospheric density profiles were calculated with a Monte Carlo code originally developed for studying Mercury's exosphere (Wurz and Lammer, 2003; Wurz et al., 2007). Exospheric densities from the observations (Heiken et al., 1991; Stern, 1999) were used as input parameters for the calculations of the altitude profiles and loss rates. Thermal release of these volatile species from the surface is used as the process to introduce them into the exosphere. Loss of exospheric species can be either by gravitational escape (Jeans escape), by photo-ionisation and photo-fragmentation, or by falling back to the surface. Return to the surface is the most common situation for the exospheric volatiles. Fig. 1a shows

density profiles for the known volatiles for the sub-solar point, i.e., these represent maximum values to be expected. The total density of the modelled volatile species sums up to $1.09 \times 10^5 \text{ cm}^{-3}$, which corresponds to a total pressure of about $1.05 \times 10^{-11} \text{ mbar}$. It is known from the Apollo missions that there is a diurnal variation in the densities of ^{40}Ar and ^4He , and likely by the other volatile species (Stern, 1999). Scale heights of the volatile species vary from 640 km for H_2 to 38 km for CO_2 (see Fig. 1a).

Photo-dissociation of molecules is a loss process for a molecular species but it is also a source process for the resulting fragment species. The hydrogen atoms in the lunar exosphere are the result of photo-fragmentation of H_2 , CH_4 and NH_3 . Fig. 1a shows the resulting H density profile. The calculated hydrogen surface density is about 8 cm^{-3} , which is compatible with earlier estimates. Fastie et al. (1973) set the upper bound of H at 10 cm^{-3} near the terminator based on an initial analyses of the data from the ultra-violet spectrometer on Apollo 17. Later, a careful reanalysis of those data by Feldman and Morrison (1991) raised the terminator limit of H to 17 cm^{-3} . Atomic hydrogen from the solar wind is generally thought to be converted to H_2 at the lunar surface.

Solar wind impinging on the lunar surface might be a direct contributor of volatile species in the lunar exosphere. Fig. 1b shows the density profiles for several such volatiles species. A special class of these volatiles are the noble gases that are implanted into the lunar soil. Assuming that the lunar soils are saturated with noble gas atoms (Schultz et al., 1978) one obtains an equilibrium between the flux of implanted solar wind noble gas ions and the flux of released noble gas atoms from the soil by diffusion. Once the noble gases are in the exosphere they stay there because they do not chemically bind to the surface. The loss processes are Jeans escape and photo-ionisation, which are calculated in the Monte Carlo code. A possible additional loss process might be cold-trapping of some noble gases in the permanently shadowed craters near the poles, which is not included in this calculation. Since the exospheric loss rates are small the noble gases are enriched in the lunar exosphere until

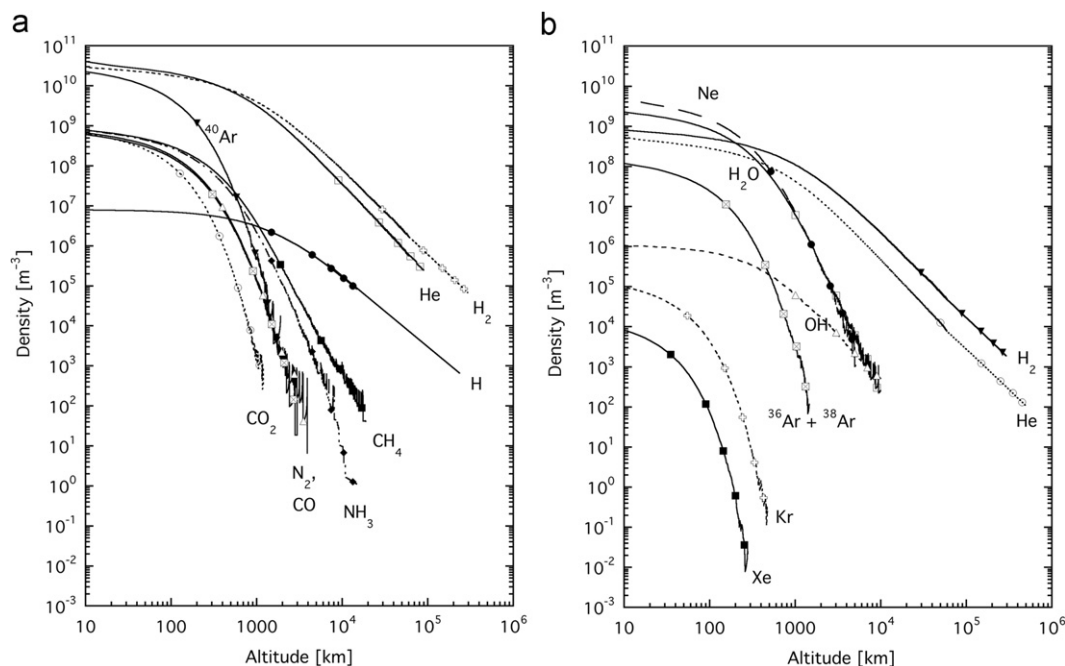


Fig. 1. Left: Density profiles in the lunar exosphere for volatile species on the dayside (at a surface temperature of 400 K) based on measurements or upper limits (Heiken et al., 1991; Stern, 1999; Killen and Ip, 1999). Right: density profiles for species related to solar wind irradiation (see text for details).

the flux of escaping particles matches the influx by the solar wind. Fig. 1b shows the density profiles for all noble gases in the lunar exosphere based on the assumption of a solar wind origin. Comparing Fig. 1a and b shows that the contribution of solar helium to the lunar He exosphere is small, with a calculated surface density of 540 cm^{-3} compared to $40,000 \text{ cm}^{-3}$ on the dayside from Apollo (Heiken et al., 1991). There is a similar situation for argon: Fig. 1a shows the ^{40}Ar density profile based on the Apollo measurements for a surface density of $30,000 \text{ cm}^{-3}$ (Stern, 1999) and Fig. 1b shows the combined ^{36}Ar and ^{38}Ar of solar wind origin with a surface density of 160 cm^{-3} . The Apollo measurements gave a $^{40}\text{Ar}:^{36}\text{Ar}$ ratio of 10:1, implying a ^{36}Ar surface density of 3000 cm^{-3} , which means that the solar wind contribution of argon to the lunar exospheric argon inventory is also small. For Ne we calculate a surface density of 4900 cm^{-3} that compares favourably with the measurements $(4\text{--}10) \times 10^3 \text{ cm}^{-3}$ (Heiken et al., 1991). For Kr and Xe there are no measurements available to compare our calculations to, there are only upper limits available, which are much larger than our predictions.

The most abundant species in the solar wind are hydrogen ions. Atomic hydrogen is chemically reactive and different chemical compounds might be the result of these reactions. For example, if all the solar wind protons are converted on the surface to H_2 molecules the density at the surface is 2100 cm^{-3} (see Fig. 1b), compared to the Apollo measurement of $(2.5\text{--}9.9) \times 10^3 \text{ cm}^{-3}$ on the dayside (Heiken et al., 1991). Since the hydrogen molecule is very light there is about 50% chance for gravitational escape and thus the hydrogen enrichment in the exosphere is small. Another chemical pathway is the formation of water molecules as a result of the proton irradiation. Zeller et al. (1970) suggested that water (and other hydrocarbons) could be formed from the solar wind protons via protolysis reactions. Already in 1972 Gibson and Moore experimentally verified the formation of water using terrestrial olivine as a lunar analogue. Recently, Managadze et al. (2011) presented experimental evidence for the formation of water on mineral surfaces under solar wind irradiation. Some water molecules will remain in the mineral compounds, but water molecules adsorbed on the surface will thermally desorb and eventually will be trapped in cold traps. In particular at equatorial and mid latitudes the surface temperature is hot enough that any produced water not confined in a mineral will evaporate immediately. Conversely, spectroscopic observations in the $\text{OH}/\text{H}_2\text{O}$ absorption band ($2.7\text{--}3.3 \mu\text{m}$) by the M3 (Moon Mineral Mapper) onboard Chandrayaan-1 show that at near polar latitudes water ice and/or hydroxyl likely exist in the lunar regolith (Pieters et al., 2009). Fig. 1b shows the water density profile under the assumption that all solar wind produced water ends up in the exosphere. With a surface density of 2900 cm^{-3} and a resulting vertical column density of $2.6 \times 10^{10} \text{ cm}^{-2}$ it is much larger than the observational upper limit of $< 1.5 \times 10^7 \text{ cm}^{-2}$. Thus, either much less water molecules are produced, or they remain trapped in the surface minerals, or they get efficiently trapped in cold locations near the poles. Managadze et al. (2011) report that the efficiency of water formation upon solar wind irradiation is about 10^{-3} for silica and olivine samples, and in earlier studies Blanford et al. (1986) found an efficiency of about 10^{-4} for several materials representative for lunar soil. After accounting for a production efficiency of $10^{-4}\text{--}10^{-3}$, the calculated water exosphere is compatible with the observational upper limit. From photo-dissociation of water there results an OH exosphere with a surface density of 1.1 cm^{-3} , and after accounting for the production efficiency water of about 10^{-3} cm^{-3} . Since the measured OH density is about 0.5 cm^{-3} (Killen and Ip, 1999), the exospheric OH has to be released directly from the surface, e.g. by sputtering from hydrated minerals, and is not the result of photo-dissociation of water.

3. The Neutral Gas Mass Spectrometer

The Neutral Gas Mass Spectrometer (NGMS) instrument is a time-of-flight mass spectrometer (TOF-MS) using a grid-less ion mirror (a reflectron) for performance optimisation. A TOF mass spectrometer has inherent advantages with respect to other mass spectrometer concepts since it allows recording of a complete mass spectrum at once without the necessity of scanning over the mass range of interest (Wiley and McLaren, 1955). This results in superior efficiency over scanning instruments (i.e., magnetic sector instruments and quadrupole mass analysers) and is particularly useful for measurements during a flyby at a planetary object where only a short time span is available to perform the measurements. Because the TOF measurement is a coincidence measurement (i.e., it is necessary to record a start and a stop signal within a short time interval), it very effectively suppresses any background in the measurements arising from UV light and penetrating radiation. Also, it is very easy to establish an absolute mass scale calibration for a TOF spectrum with high accuracy (e.g. Scherer et al., 2006). Additionally, the mechanical design of a time-of-flight mass spectrometer is quite simple, which is favourable for an implementation in space flight.

The NGMS instrument is based on the design of the P-BACE instrument (Abplanalp et al., 2009). A photograph of the P-BACE instrument inside a glass enclosure is shown in Fig. 2, where the ion source, the time-of-flight path, the ion mirror, and the detector can be seen. As can be seen, these elements have a moderate level of complexity, which is favourable for a realisation for an instrument for space research. Prior to the P-BACE instrument a similar version was built for our noble gas research laboratory. The P-BACE instrument ion-optical design has been successfully verified by testing it on a stratospheric balloon campaign in summer 2008 where the instrument recorded about 4500 mass spectra during this 5-day flight in the circumpolar wind pattern existing during northern summer (Abplanalp et al., 2009; Wieser et al., 2009). The improvements of the present NGMS instrument over the P-BACE design are two-fold: first, we accomplished a significant improvement of the ion-storing capability of the storage ion source (Abplanalp et al., 2010), and second, we optimised the signal pickup at the ion detector and the front-end electronics of the signal acquisition. The two measures together resulted in a lowering of the detection threshold by two decades and improved the mass resolution at low masses. Sample mass spectra demonstrating the present performance are shown below.

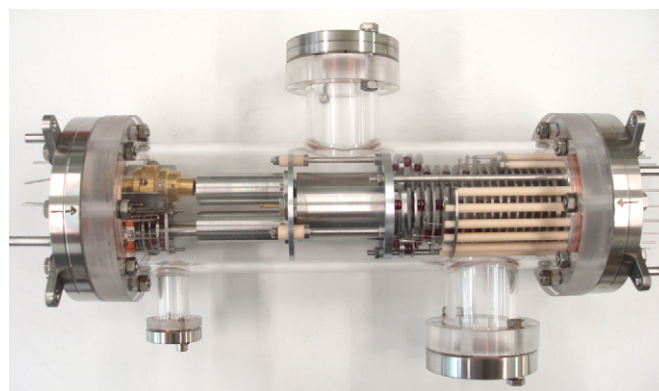


Fig. 2. The P-BACE NGMS instrument is shown, accommodated in a glass structure for better visibility of the ion optical elements. The ion source and the detector are located on the left side, with the latter being the gold-plated structure. In the middle are the drift tubes, and on the right is the ion mirror, a stack of potential rings, for energy focussing.

The NGMS design also benefits from heritage from the RTOF sensor of the ROSINA instrument on the Rosetta mission (Scherer et al., 2006; Balsiger et al., 2007). The mechanical dimensions of the RTOF sensor are $114 \times 24 \times 38 \text{ cm}^3$ (length $\times$ depth $\times$ height) with a total mass of 14.7 kg; the present NGMS design is much smaller and lighter than RTOF, as discussed below. In any case, sufficient resources for a RTOF size instrument are presently not available on either of the two spacecraft. Currently, a flight version of the NGMS instrument is being developed for the Luna-Resurs and Luna-Glob missions of the Russian Space Agency, Roskosmos, which will land on the lunar south and north pole, respectively (Khartov et al., 2011). The mass spectrometers will be coupled to a gas-chromatograph (GC) system to analyse the volatile content of lunar soils, the so-called GC–MS complex. In addition, these mass spectrometers can also directly sample the lunar exosphere to study its composition.

Ions are generated in an ion storage source we developed over the last years (Abplanalp et al., 2010). Ionisation is by electron impact from ambient gas inside the ion source. The ambient gas is from the output of the gas-chromatographic system (GC-mode) provided via heated 1/32" OD standard tubing directly to the ionisation volume of the ion source (see Fig. 5). When the GC system is not operating the ambient gas is from the lunar exosphere (exosphere mode) via the exhaust tube of the mass spectrometer that connects the instrument to the outside of the

spacecraft (see Fig. 5). Since the lunar exosphere is a very thin atmosphere, as discussed above, the ion source has to be operated in the exosphere mode with significantly higher sensitivity for the measurement of exospheric gas. For this mode background gas from the spacecraft might pose a serious limitation to investigate the tenuous lunar exosphere. Even with spacecraft being a long time in interstellar space the outgassing from the spacecraft can still be recorded Schläppi et al., (Mall) (Schläppi et al., 2010).

With the pulsed ion optics of the ion source ion packets are produced, accelerated, shaped and sent onto the TOF path of the mass spectrometer. The repetition rate of the pulsed ion optics, and thus the cadence of recorded mass spectra, is typically in the range 1–10 kHz. Ion packets separate along the TOF path according to their mass-per-charge ratio because they are accelerated to the same energy per charge (within small uncertainties). After passing the first leg of a field-free drift path ions are reflected by the ion mirror, which allows for energy and spatial focussing of ions, and directed onto a fast micro-channel plate detector. On a fast ion detector the mass-per-charge packets are converted to electron charge pulses that are recorded with an ADC or a TDC signal acquisition system. Typically, 10,000 to 100,000 mass spectra are accumulated to a histogram to increase the dynamic range to 7 decades and more. Depending on repetition rate and number of accumulations, a full mass spectrum is available after 1–100 s. This recorded time-of-flight spectrum is easily converted into a mass spectrum.

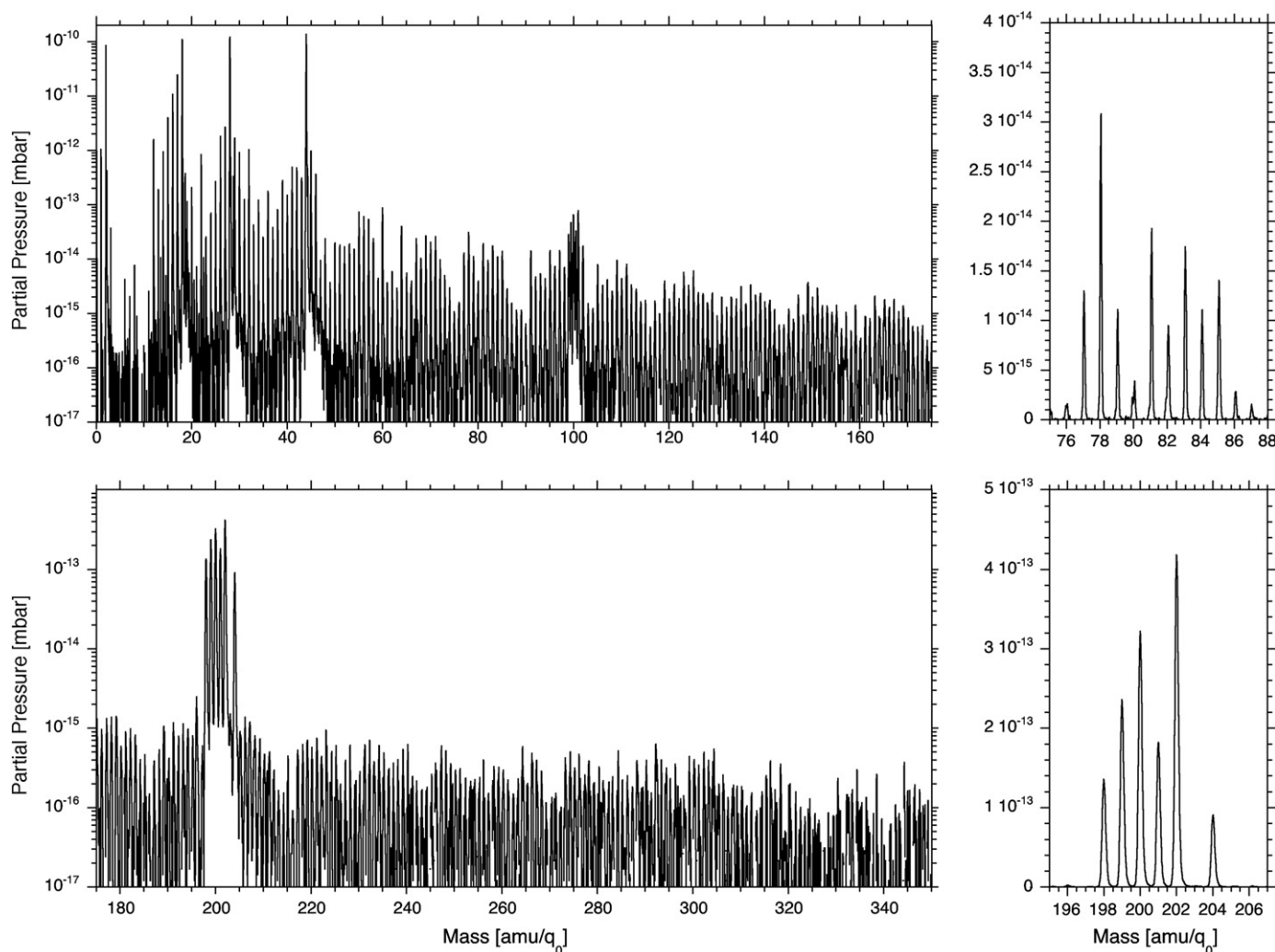


Fig. 3. Mass spectrum of residual gas recorded at a total pressure of 5.0×10^{-10} mbar. Background level of 1.0×10^{-16} mbar is routinely reached in such measurements. Small panels on the right show details around mass 82 amu, and the Hg isotope pattern, with mass resolution of about 1000.

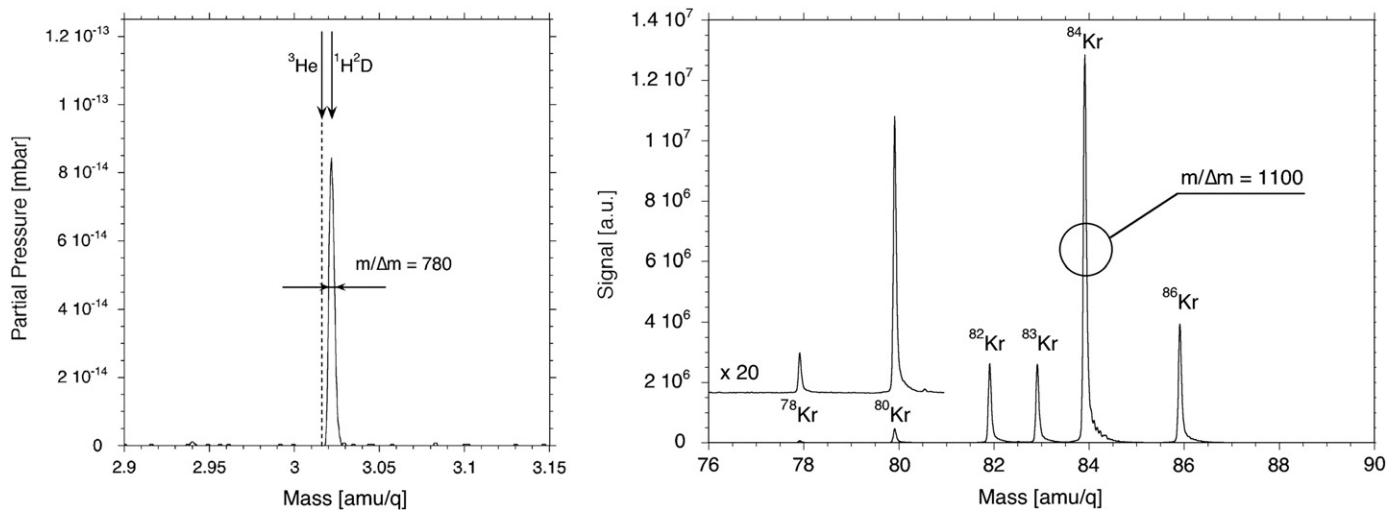


Fig. 4. Left: Detail around mass 3 amu, showing the HD line from a residual gas mass spectrum recorded with the prototype instrument at 5.4×10^{-10} mbar, and the expected position of ^3He . Right: Figure shows a section of a mass spectrum recorded at a total pressure of 2×10^{-9} mbar when Krypton gas was introduced into the chamber.

Source: Abplanalp et al., 2009 (right panel).

The NGMS instrument has a mass range of 1000 amu. In principle, the mass range is only limited by the size of the data acquisition memory. Constraints on the useful mass range arise from the mass resolution and the ability of the ion source to generate ions of high mass. Fig. 3 shows a residual mass spectrum from a vacuum at a total pressure of 5.0×10^{-10} mbar recorded in 65 s at a repetition rate of 1 kHz. A background level of 1.0×10^{-16} mbar (corresponding to a density of about 1 cm^{-3}) is routinely reached in such measurements. Therefore, even at a total pressure of only 10^{-10} mbar a dynamic range of 6 decades is accomplished. With longer integration times and/or larger repetition rates larger dynamic ranges will be achieved. The flight version of the signal acquisition records the mass spectra at a rate of 10 kHz, thus the mass spectrum shown in Fig. 3 is recorded in less than 10 s.

With the ADC signal acquisition system NGMS has a mass resolution of about $M/\Delta M=400$ at mass 3, which increases to $M/\Delta M=1100$ at higher masses. Fig. 4, right panel, shows a measurement, where Kr has been introduced into the system at a pressure of 2.0×10^{-9} mbar and all the Kr isotopes are clearly resolved. Other examples are shown in the insets of Fig. 3. With the TDC signal acquisition system the mass resolution is higher, at the expense of dynamic range. At mass per charge 3 a mass resolution of $M/\Delta M=780$ is reached (see Fig. 4, left panel) that allows the direct separation of $^1\text{H}^2\text{D}$ from ^3He ions in the mass spectrometer, which is of considerable scientific importance.

The implementation of the scientific scope for the mass spectrometer for the Russian lunar missions requires a mass range of 200 amu and a mass resolution of $M/\Delta M > 400$, which is easily met by the NGMS instrument. The present design of the NGMS flight instrument for the Russian lunar missions is shown in Fig. 5. The NGMS flight design is similar to the RTOF design: in that the sensor is mounted on top of the electronics box. The latter contains all the NGMS electronics, but the high-voltage pulsers, which are located close to the ion-optical element to be pulsed to minimise the need for electrical power. The ion source (yellow unit on the left in Fig. 5) and the ion mirror (grey unit on the right in Fig. 5) are brazed metal–ceramic composites, technologically the same as used for RTOF. To the drift tube (yellowish structure in the centre) connects the exhaust tube, which facilitates evacuation of the instrument to the outside of the spacecraft, thus directly connects to the lunar exosphere. NGMS linear dimensions are approximately $245 \times 145 \times 176 \text{ mm}^3$ (length $\times$ depth $\times$ height),

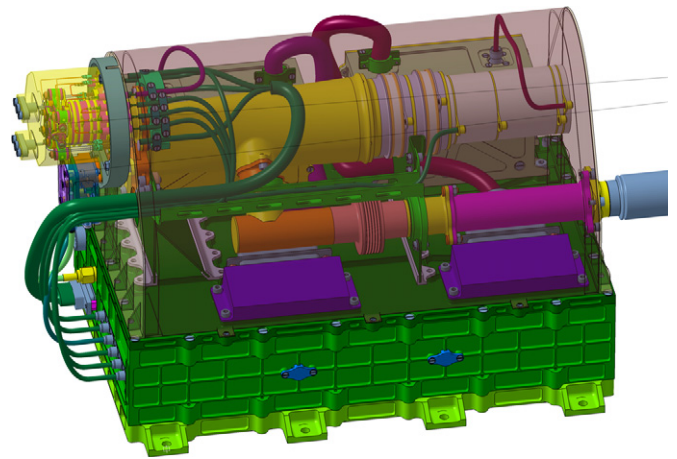


Fig. 5. Design of the NGMS flight instrument for the Luna-Resurs and Luna-Glob missions. The sensor cover is shown semi-transparent in this display to show the sensor structure. On the housing of the ion source (yellow unit on the top left) the inlet and outlet connectors for the gas tubing for the GC output can be seen. The grey-blue pipe at the right (truncated in this image) is the exhaust pipe for evacuating the instrument toward the lunar exosphere.

its mass is 3.5 kg, and its power consumption is 17 W, maximum, when acquiring mass spectra from the GC samples, and 9 W when acquiring mass spectra from the lunar exosphere. For acquiring mass spectra from GC samples a repetition rate of 10 kHz will be used to optimise the cadence of spectra and their dynamic range. For acquiring mass spectra from the lunar exosphere a repetition rate of 1 kHz will be used to save power, and the dynamic range will be accomplished by longer integration times.

4. Conclusions

The lunar exosphere is very tenuous and mostly consists of volatile species, as discussed above, with a small contribution from refractory elements from the soil via solar wind sputtering (Wurz et al., 2007). Since each volatile species has its own origin and history, a lot about the Moon can be learned from the mass spectrometric analysis of the lunar exosphere and the volatile content in the soil (Wurz et al., in press). The mass spectrometric

analysis of the volatile content in the soil will be realised on the Luna-Resurs and Luna-Glob missions, with NGMS being part of the GC-MS complex. Also, measurement of the composition of the lunar exosphere will be attempted. This measurement might be difficult because of interferences from spacecraft outgassing and from the remainder of the plume of the retro-rockets needed for landing the spacecraft, which will release to the ambient atmosphere an amount of gas that increases the total mass of the lunar exosphere by about 30% (Stern, 1999). Thus, it is better to measure the composition of the lunar exosphere from orbit. Since the scale heights are quite large (see Fig. 1) already an orbit with altitude of 100 km measurements with the NGMS instrument would allow covering most of the volatile species. A spacecraft altitude of 30 km would be preferable so that good mass spectrometric measurements can be accomplished also on the night side. If the orbital measurements of exosphere can be conducted during the landing of an other spacecraft on the lunar surface the amount and chemical composition of the contamination of the lunar exosphere by the gases from the landing spacecraft can be studied directly. This would be highly interesting in view of the reported plans for lunar landings by several space agencies in the next decade.

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