






RESEARCH ARTICLE

EGT—A sensitive time-of-flight mass spectrometer for multielement isotope gas analysis

Andreas Riedo^{1,2}  | Surya Rout²  | Reto Wiesendanger²  | Peter Wurz²  | Ingo Leya² 

¹Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, Leiden, The Netherlands

²Space Research and Planetary Sciences, Physics Institute, University of Bern, Bern, Switzerland

Correspondence

Andreas Riedo, Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, Leiden, The Netherlands.
Email: riedo@strw.leidenuniv.nl

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Abstract

The principles of operation and figures of merit of a novel, compact (324 mm × Ø 114 mm; volume approximately 1000 cm³) reflectron-type time-of-flight mass spectrometer designed for simultaneous multielement isotope gas analysis is presented. The system, which consists of a pulsed electron impact ion source, is designed either to directly analyse gas samples collected and stored in a compartment or samples extracted from solids using a CW laser system (fibre-coupled diode laser, <75 W, $\lambda = 808 \pm 10$ nm). In latter case, laser pulses are focussed onto the sample surface to spot sizes of approximately 400 μ m in diameter that allows for direct ablation and vaporisation of solid sample material and releasing of trapped gases. A cleaning and trapping system that consists of various cold stages and getters is used before the gas enters the mass analyser. Measurements on various gases were conducted for performance evaluation, ranging from standard gases (Ar, Kr, and Xe) to trapped gases extracted from a sample of the Millbillillie meteorite. At optimised instrument settings, mass spectrometric measurements can be conducted with a mass resolution $m/\Delta m$ of up to approximately 1200 (¹⁶O and CH₄ can be resolved), with a dynamic range of approximately 6 orders of magnitude and a mass calibration accuracy of approximately 100 ppm. The high detection sensitivity of the system allows the detection of gas species at partial pressures down to the low 10⁻¹⁶ mbar level (corresponding to <10 particles/cm³ at standard temperature and pressure, including an ion transmission of approximately 80%). Measurements using standard gases demonstrated that the isotope ratios for a given element can be measured with an accuracy at the per mill level (relative to terrestrial values). Measurements of Ar extracted from the meteorite Millbillillie gave a ³⁶Ar/³⁸Ar ratio of approximately 1.6, which is in good agreement with literature values.

KEYWORDS

compact time-of-flight mass spectrometer, multielement isotope analysis, noble gas, sensitive gas analysis, space research

1 | INTRODUCTION

Mass spectrometric instruments designed for gas composition analysis (elemental and isotopic) providing a high detection sensitivity coupled

with the capability of simultaneous multielement analysis are of high interest and often mandatory in various fields of scientific research, ranging from, eg, in situ chemical analysis of planetary atmospheres^{1,2} and exospheres,³ analysis of volatile species in the lunar soil,⁴

composition analysis of volcanic gases,⁵ to noble gases that are extracted either from meteorites or Earth surface rocks.^{6,7} Especially in the field of noble gas (He, Ne, Ar, Kr, Xe) mass spectrometry, instruments having a high detection sensitivity and ionisation efficiency are mandatory as the investigated solid samples are typically highly depleted in these gases. Since the introduction of the concept of measuring in static operational mode that allows to measure small quantities of a gas (introduced by Reynolds⁸ and Aldrich and Nier⁹ around the 1950s), there is a continuous request for instrumentation with improved figures of merit and measurement capabilities.^{10–14} To date, various systems were designed and developed in noble gas mass spectrometry with the goal to improve measurement capabilities, ranging from quadrupole mass spectrometers,¹⁵ resonant ionisation mass spectrometers,^{16–18} mass spectrometer that are coupled to a compressor,¹² among others. Sector field mass spectrometers coupled to multicollector systems are today's state-of-the-art laboratory techniques used in noble gas mass spectrometry as they provide the most accurate isotope ratio analysis.^{10,19–21} However, aside of their undoubted measurement capabilities, these systems are typically designed and optimised for one or a few noble gases and other specific element isotopes only. For the analysis of precious and limited available sample material, such as rare meteoritic samples and extra-terrestrial samples from sample-return missions, sensitive and quantitative instrumentation with multielement isotope analysis capabilities are of interest because such instrumentation allows to address a scientific question from various, complementary sides.¹⁷ This still holds even if such instrumentation do not show the same measurement accuracy on element isotope ratios as the state-of-the-art sector field instrumentation.

In this contribution, we present the figures of merit and the measurement capabilities (detection sensitivity, mass resolution and accuracy, ionisation efficiency, and element isotope ratio analysis) of a novel, compact reflectron-type time-of-flight (TOF) mass spectrometer (instrument name EGT, historically named EdelGas Time-of-flight) designed for sensitive multielement isotope gas analysis as a complementary instrument to state-of-the-art instrumentation. For the characterisation of the instrument performance, measurements were conducted using noble gases from specially prepared standard reservoirs, Ar extracted out of a sample of a meteorite, and using the residual gas within EGT's vacuum chamber.

2 | EXPERIMENTAL

2.1 | Gas samples

For the performance characterisation of the EGT, the residual gas within its vacuum chamber (typical base pressure of approximately 1×10^{-10} mbar, all electronics on), three standard gases (Ar and a mixture of Kr and Xe, all stored in external reservoirs with a total volume of approximately 1000 cm³ and a pipette size of approximately 1 cm³ connected to the EGT), and laser extracted Ar from the meteorite Millbillillie^{22–24} (approximately 3.5–4.0 mg) were analysed. The eucrite meteorite Millbillillie is very well characterised and is generally used as a calibration standard. For the standard gases, a defined

volume of Ar (4.12×10^{-7} cm³STP, corresponding to approximately 1.1×10^{13} atoms; accuracy, approximately 0.5%) and a mixture of Kr/Xe (Kr: 2.16×10^{-10} cm³STP, 5.8×10^9 atoms; Xe: 2.21×10^{-10} cm³STP, 5.9×10^9 atoms; both with an accuracy of approximately 0.8%) is used for analysis. All three standard gases are of atmospheric isotope composition.¹⁴

2.2 | Environment

The experimental set-up is located in a temperature-controlled laboratory; the nominal temperature and relative humidity is $22 \pm 0.5^\circ\text{C}$ and $40 \pm 5\%$, respectively. The dust filtered laminar flow over the entire surface area does not only guarantee stable conditions for the operation of the instrument, it also allows proper sample handling, ie, sample preparation and loading the sample into the laser extraction unit.

2.3 | Experimental set-up and principles of operation of the EGT

The multielement isotope gas analyser is a compact (324 mm \times \varnothing 114 mm; volume, approximately 1000 cm³) reflectron-type TOF mass spectrometer. The design is based on extensive ion trajectory

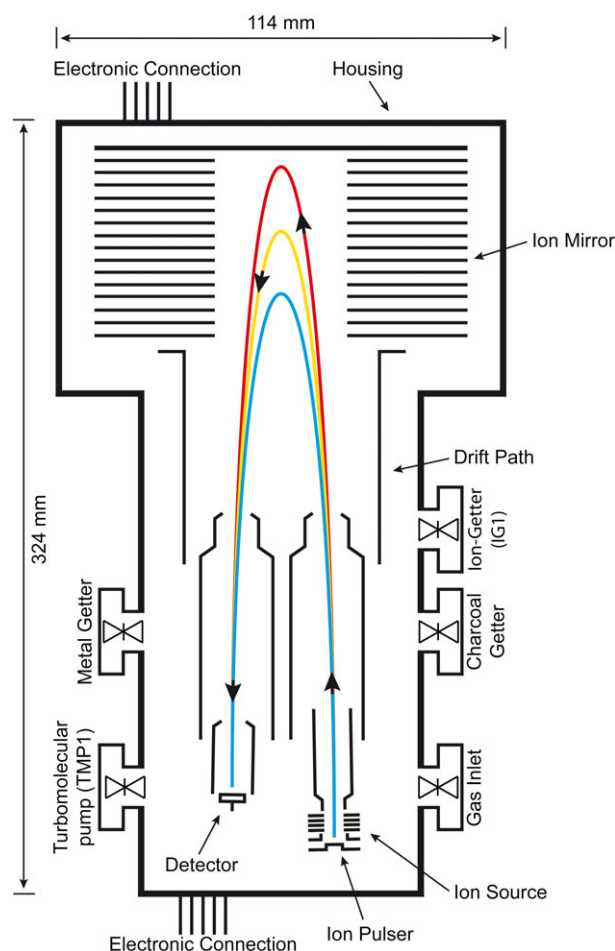


FIGURE 1 Schematic drawing and principles of operation of the EGT. The gas enters the instrument through the gas inlet valve. At the electron impact ion source, the gas is ionised and pulsed into the mass analyser after passing through the ion source optics. After passing the field-free drift path, the ions are reflected at the ion mirror towards the detector system and passing a second time the drift path

simulations using the software SIMION (Scientific Instrument Services, Inc, USA), and the instrument was built in-house to utmost ultra-high vacuum (UHV) standards.

Figure 1 shows the schematics and principles of operation of the instrument. The system has five gate valves, including two towards the pumping system, one for the gas inlet, and one for a cold trap containing activated charcoal for freezing Ar and CO₂ during He–Ne measurements because both gases would produce double charged interferences on ²⁰Ne and ²²Ne, respectively. The fifth gate valve connects the spectrometer to a metal getter (SAES®) to reduce the H₂ background in the spectrometer because high H₂ amounts would naturally result in high ¹H–²H amounts, which interferes with the ³He signals. The pumping system connected to the EGT consists of an ion getter pump (IG1) and a turbomolecular pump (TMP1). The latter is pumping to a reservoir (RES1), which is evacuated from time to time (if $p > 10^{-2}$ mbar) by a turbomolecular pump, which is connected to a four-chamber membrane pump (RVTMP). Because the system is designed for low gas amounts, the EGT is not actively pumped during measurements (static mode).^{8,12} After a measurement, the remaining gas is evacuated by TMP1 to prevent contamination of IG1. The gate valve to IG1 is only opened if the system is in standby mode. In standby mode, the valve to TMP1 is closed to prevent venting the system in case of a pump breakdown. The gate valve for gas inlet is connected to a cross made of standard vacuum components, which is connected to the reservoirs of the standard gases and to a laser ablation set-up, which allows gas extraction from solid silicate materials (discussed later). The cross is evacuated by a second turbomolecular pump (TMP2), which is also pumped into a reservoir (RES2). This reservoir is connected to the same pump system (turbomolecular pump and RVTMP) as the reservoir of the EGT. Once the sample gas is introduced into the cross piece, the gate valve of the gas inlet is opened for 5 minutes to guarantee pressure equilibration. After the 5 minutes, the gate valve is closed and the remaining gas in the cross piece is pumped (TMP2).

A pulsed and emission controlled electron-impact source is used for ionisation of the gas species. In the current design, we use a commercial lanthanum-hexaboride (LaB₆) single crystal as an electron emitter, which is mounted on a carbon wire (Kimball Physics Inc, USA) and operated and kept at a constant emission current of 250 μ A. To ensure optimal working conditions, ie, a stable temperature and no risk of contamination, the filament is always operated at a constant emission current. Once the gas is ionised, the ions are pulsed into the ion optics of the system. The repetition frequency of the pulser can be adjusted (≤ 10 kHz; rise time, approximately 4.6 ns) for optimal measurement conditions. Note that the lower the pulse frequency, the more ions can be stored in the ion source.²⁵ However, a longer storage time of the ions in the source region can also result in unwanted nonlinear effects, ie, detector saturation, sensitivities, or fractionation factors that depend on the gas amounts.

First, the ions pass the ion optics for acceleration, focussing, and confinement before entering the field-free drift region for mass separation. At the girdless ion mirror, the ionised species are reflected towards the detector system and finally they pass a second drift path. The ions sequentially arrive at the detector system, according to their mass over charge ratio (TOF measurement principle). The in-house

designed detector system consists of multichannel plates (MCP, chevron configuration, quality diameter of 8 mm) for the generation of electric signals and an anode of Apollonius design for collecting the generated electron avalanches.^{26,27} A high-speed analogue-to-digital converter (ADC) card (two channels, max. sampling rate of 3.2 GS/s, 12 bit, U5303A, Acqiris, Switzerland; former Keysight and Agilent) is used for recording TOF spectra on the host computer. An in-house designed software is used for data analysis, including conversion between TOF to mass spectra, integration of signals, accumulation of TOF spectra, among others. A detailed description of the software can be found in one of our previous publications.²⁸

2.4 | Laser ablation extraction system

The laser extraction line is designed for the extraction and cleaning of small amounts of gas from solids, mostly silicate materials. The line can be divided in two main parts: (1) the laser extraction part and (2) a gas cleaning part. The entire line is evacuated using a turbomolecular pump (TMP3) connected to a reservoir (RES3), which is again from time to time (if $p > 10^{-2}$ mbar) evacuated using the turbomolecular pump/RVTMP system (see also above). The extraction laser is a CW fibre-coupled diode laser (<75 W, $\lambda = 808 \pm 10$ nm). The output power can be controlled remotely to optimise ablation or melting of the sample. The laser system is positioned outside the vacuum set-up, and the laser beam is pointed towards the sample with a beam diameter of approximately 400 μ m. A red guidance pilot laser helps in targeting and navigating the laser on the sample. The sample and the laser ablation is viewed in real time using an attached video camera. The temperature achieved during the laser ablation is measured using a well-calibrated two-colour pyrometer. Samples are placed in cavities on a custom-built sample holder, which is installed in an all metal vacuum chamber except for the viewport on top, just below the laser. In Figure 2, a region of the powdered Millbillillie meteorite is shown before and after laser ablation. After laser melting at approximately 2000°C, the silicate minerals transform into a glassy form because of the rapid cooling, which is a clear indication for melting the sample.

The gas extracted during laser ablation passes first through a U-shaped stainless-steel carrier line that is cooled with liquid nitrogen to freeze-out water. Adsorbed water is abundant in the investigated powdered Millbillillie meteorite and also typically in other silicate mineral samples. Next, the gases cleaned of water passes through a cross piece at which two metal getters (SAES®) and two cold traps filled with activated charcoal are connected. At the working temperature of 280°C, the getters efficiently clean the gas from nitrogen and hydrocarbons. The two activated charcoals can be cooled to temperatures in the range of either -100°C to -135°C or -196°C for selective trapping of Kr–Xe and Ar, respectively. During the studies presented here, none of the cold traps were used. After laser melting, we wait 10 minutes for gettering and gas equilibration before the gas is introduced into the cross piece that is directly connected to the EGT (see above).

2.5 | Measurements

A typical measurement run consists of (1) a measurement of the background of the EGT in static operational mode and (2) a measurement

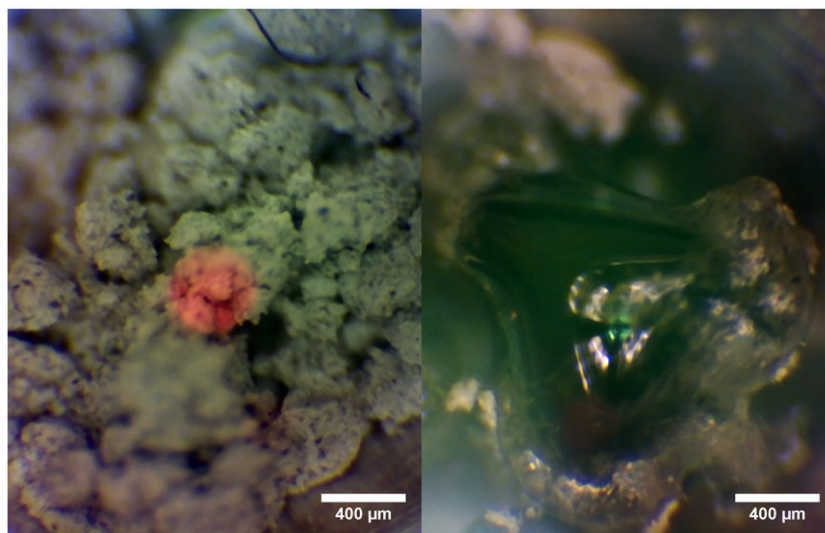


FIGURE 2 Real-time imaging of the sample allows to optimise laser ablation and evaporation of sample material. Left: The pilot laser spot in red (400 μm in diameter) is used for targeting the raw material (here, a sample of the meteorite Millbillillie). Right: Sample material after laser ablation [Colour figure can be viewed at wileyonlinelibrary.com]

of the sample gas. The background signals are subsequently subtracted from the signals of the sample gas. For calibration purposes, standard gases can be measured before and after the measurements. Between each measurement, all the vacuum compartments are evacuated to the typical base pressures. During a typical measurement run, several 10 000 to 100 000 TOF spectra are recorded. Similar to studies using another set-up,^{29,30} the spectra are accumulated on board the ADC card to several thousand before saving the accumulated spectra on the host computer. This procedure allows real-time monitoring of the measurement stability during a measurement campaign.

3 | INSTRUMENTAL PERFORMANCE AND DISCUSSION

3.1 | Sensitivity

Figure 3 depicts a measurement of the residual gas within the EGT ($p_{\text{tot}} = 1.1 \times 10^{-10}$ mbar, gate to TMP1 open, gate to IG1 closed).

The measurement consists an accumulation of 10^6 TOF spectra in total (500 accumulated files, each consists of 2000 spectra). For the conversion of recorded signals to partial pressures, we assume that the pressure measured by the cold-cathode gauge that is directly connected to the EGT is given by the four major peaks in the mass spectrum, ie, H_2 , H_2O , CO , and CO_2 . The left panel of Figure 3 shows an overview spectrum of the mass range (m/z) 1 to approximately 230. Interestingly, the isotopes of Hg with a maximum partial pressure of 10^{-14} mbar can easily be observed (^{202}Hg with approximately 500 particles/ cm^3STP). Currently, the source of the Hg is unknown as only certified materials without any known Hg impurities were used for construction. However, the detected partial pressure of Hg is very low and even a minor contamination during manufacturing could be the reason. Such a contamination could be, eg, by using tools that were in contact with, eg, soldering wires, which are known to contain trace abundances of Hg. Interestingly, the amount of the Hg contamination could not be reduced even after several bake-outs of the vacuum system (approximately 200°C for several days); the signal stayed constant. On the right panel of Figure 3, the mass range of approximately 165 to 185 is shown in more detail. It can be seen that ion

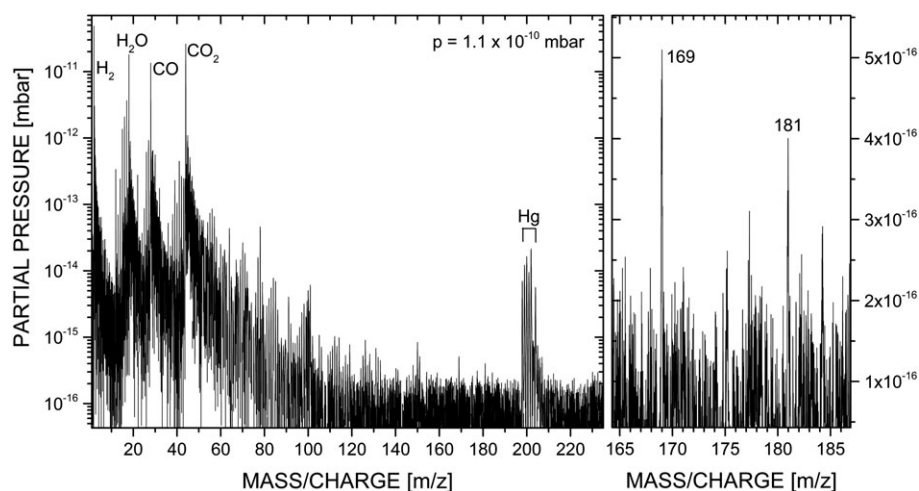


FIGURE 3 Measurement of the residual gas in the EGT. The total pressure as measured with a cold-cathode gauge was approximately 1.1×10^{-10} mbar. The detection sensitivity of the instrument allows measuring partial pressures down to the lower 10^{-16} mbar level

species with partial pressures $>3 \times 10^{-16}$ mbar can be detected. With an ion transmission of approximately 80% (derived from SIMION simulations), less than approximately 10 particles/cm³STP can be detected in an integration time of approximately 1850 seconds. The sufficiently high mass resolution and accuracy of the mass scale calibration (discussed later) allows distinguishing between “real” mass peaks and electronic or captured noise peaks. Real peaks only appear at full numbers (at least close to, given the actual mass and assuming only single charged ions); a peak appearing between two entire (m/z) values would be considered as a noise peak.

The measurement of the residual gas allows furthermore to define the dynamic range of the system (left panel of Figure 3). The simultaneous measurement of gas species with partial pressures in the range from high 10^{-11} mbar to low 10^{-16} mbar points to a dynamic range of about 6 orders of magnitude.

3.2 | Mass resolution

Figure 4 shows the mass resolving power $m/\Delta m$ of the EGT as a function of the mass over charge ratios (m/z) of the detected ion species. We used the mass spectrum shown in Figure 3 for the mass calibration. At low (m/z) values, ranging from H to about O, the mass resolution increases with increasing (m/z) up to a value of approximately 800. This trend is limited due to electronic interferences with the pulser, which has a rise time of approximately 4.6 ns (see red dashed line). After the steep trend, the mass resolution still increases with increasing (m/z) to values of approximately 1200, though the slope is shallower.

A mass resolution of approximately 800 achieved already at (m/z) values lower than approximately 20 allows the simultaneous detection and identification of ^{16}O and CH_4 (see top panel of Figure 5). Depending on the scientific question, this performance could be of interest as the abundance of both peaks can in principle be quantified using a multipeak fit function. At (m/z) values of single charged Hg, a mass

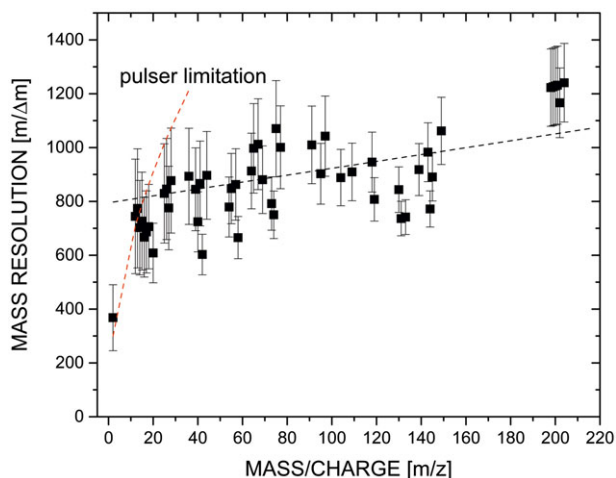


FIGURE 4 Mass resolution $m/\Delta m$ of the EGT as a function of the mass/charge (m/z) ratio. In the mass range below approximately 16, the mass resolution is limited by electronic interferences with the pulser (dashed line in red). After the rise-time of the pulser, the full mass resolution of up to 1200 can be reached [Colour figure can be viewed at wileyonlinelibrary.com]

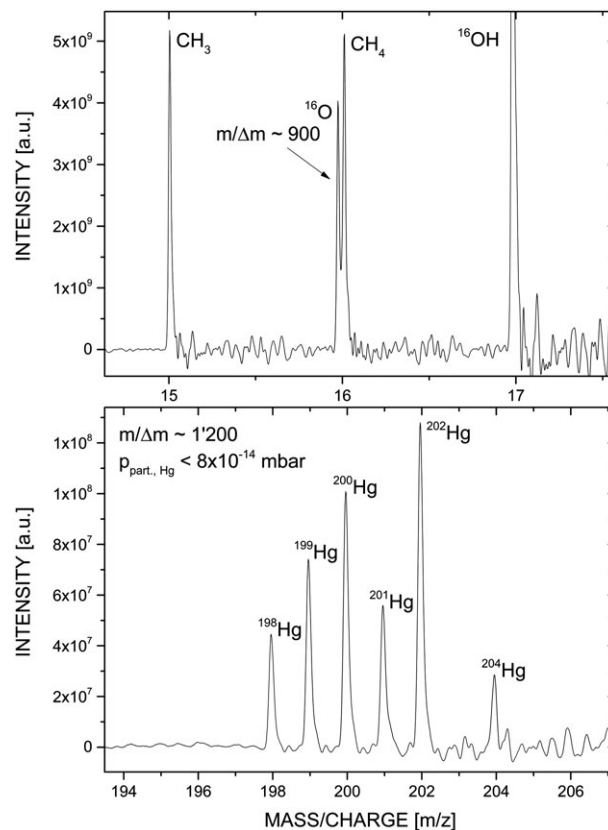


FIGURE 5 Parts of a mass spectrum showing the signals in the mass range around ^{16}O (top panel) and Hg (bottom panel). The steep increase of the mass resolution $m/\Delta m$ (see Figure 4) allows to separately detect ^{16}O and CH_4 . At high mass/charge ratios, the Hg isotopes can be detected with a mass resolution of approximately 1200

resolution of approximately 1200 is reached (see bottom panel in Figure 5). Remarkably, the detected Hg isotope peaks with a partial pressure of approximately 8×10^{-14} mbar and lower (see also Figure 3) are all sufficiently separated, which allows reliable isotope ratio analyses (see discussion in Section 3.6).

3.3 | Detector system—Single ion event measurements

The detector system consists of two MCP plates (chevron configuration, Photonis USA, Inc, USA) for detecting the ions and generating electron avalanches and an anode of Apollonius design, both designed in-house. The MCPs used in this configuration have a quality diameter of 8 mm, a pore diameter of 10 μm , a pitch of 12 μm , a bias angle of 8°, and an L/D ratio of 60:1.

For the performance characterisation of the detector system, including speed and signal amplification of incoming ions, single ion event measurements were performed at different gain levels, with a similar procedure as discussed in Schletti et al.³¹ Multichannel plates operating voltages in the range of $\Delta V = 1700$ to 2000 V were applied to the MCP stack (ΔV = voltage front MCP – voltage back MCP). The voltage was increased stepwise by 50 V. During measurements, the voltage at the back of the MCPs was kept constant at -300 V, which give the best electronic connection between the back

of the MCP stack and the Apollonius anode. At each MCP operating voltage, 4 to 10 individual measurements were conducted. A digital phosphor oscilloscope (DPO) with a high sampling rate and a high bandwidth (BW) was used for single ion event detection (Tektronix, DPO 7354c, 40 GS/s, 3.5 GHz BW). Therefore, the DPO offered a higher sampling rate and a larger BW than the ADC card typically used. For the measurement of single ion signals, only the detector system was switched on (ion optics and ion source were switched off), and the system was pumped actively by its TMP1, ie, the gate valve to IG1 was closed. The base pressure during the measurements was approximately 1.9×10^{-11} mbar. Positively charged ions that were either produced in interactions of cosmic rays and/or from the cold cathode gauge connected to the ETG were used for this measurement.

The left panel of Figure 6 displays the correlation between signal intensities and the full width measured at half maximum (FWHM) of detected single ion events. It can be seen that the FWHM increases with increasing signal intensities. At the lowest signal intensity, a FWHM of approximately 650 ps was measured; the value reaches approximately 1 ns at the highest intensities. In addition, the expected trend of increasing signal intensities with increasing operating voltage is also visible (see colour-coded symbols). At an MCP operating voltage of $\Delta V = 2$ kV, a large signal of approximately 200 mV is recorded for a single ion detection. On the right panel of Figure 6, a measurement of a single ion event recorded with $\Delta V = 1700$ V is shown. The peak with an amplitude of about 25 mV is very symmetric with a FWHM of 736 ps and a fast falling time of 226 ps (BW corrected).^{27,31}

In comparison with our previous publication, in which we discussed an MCP detector system coupled to a segmented anode of microstrip design (FWHM down to 250 ps and falling times down to approximately 170 ps, BW corrected),³² the system discussed in this contribution shows larger FWHMs and slightly increased fall times. However, the efficient electron capture of the Apollonius anode, which is more than two times higher than in the previous study, is one of the reasons why the EGT has a high detection

sensitivity down to the 10^{-16} mbar level. Furthermore, the observed increased FWHM is not compromising the instrument performance because the FWHM is currently not limiting the observed mass resolving power of the EGT. However, the FWHM could easily be improved (rising edge) and is planned in the future by, eg, adding capacitors near the detector system, allowing for a fast recharging of the MCP's.³² Currently, the integration of electric components inside the EGT is kept at minimum to guarantee very low outgassing and therefore low base pressures, which is required for reliable measurements of very low gas amounts.

3.4 | Ionisation efficiency

The ionisation efficiency of the EGT can be characterised by studying if and by how much the signal of the gas species of interest is decreasing. Figure 7 depicts the ^{40}Ar signal (calibration gas) as a function of the measurement time. In this measurement campaign, more than 2500 accumulated spectra were recorded and saved on the host computer, each consisting of 2000 single spectra (giving 5×10^6 recorded spectra in total); the acquisition lasted 8804 seconds (about 2 h and 27 min). Within this measurement period, the ^{40}Ar signal decreases by approximately 16%. Physically, the decrease must be exponential. However, for small gas usages, the exponential behaviour can well be approximated using a linear relationship. For comparison, the decrease of ^{40}Ar in a sector field mass spectrometer (MAP 215-50, 90°, 15 cm radius) routinely used in our laboratory is 90% in 2.5 hours. This slow signal decrease, in comparison with the MAP instrument, is of high interest as the measurement accuracy increases with the increase of measurement time, corresponding to an increase of number of recorded spectra (see following Section 3.6).

3.5 | Mass calibration accuracy

For the conversion between TOF and mass spectra, we use a quadratic equation of the type $(m/z)_i(t) = k_0(t_i - t_0)^2$, where i is an index of an identified peak of an isotope or molecule and k_0 and t_0 are fit-

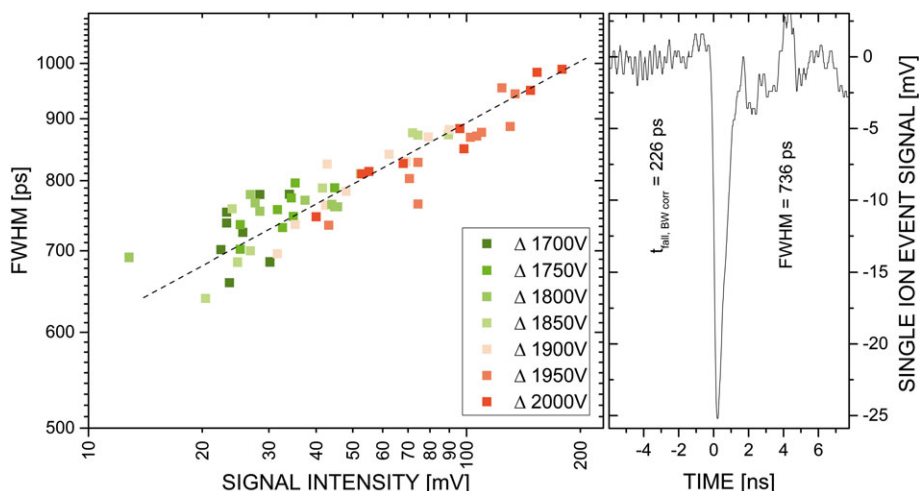


FIGURE 6 Left: Correlation between detected signal amplitudes and pulse widths (full width measured at half maximum [FWHM]) of single ion events at various applied potential differences ΔV over the multichannel plate stack in the range of 1.7 to 2.0 kV. Right: Detected signal of an ion single event. A FWHM of 736 ps and a bandwidth corrected fall time (10% to 90% level) of 226 ps was measured at a peak amplitude of about 25 mV [Colour figure can be viewed at wileyonlinelibrary.com]

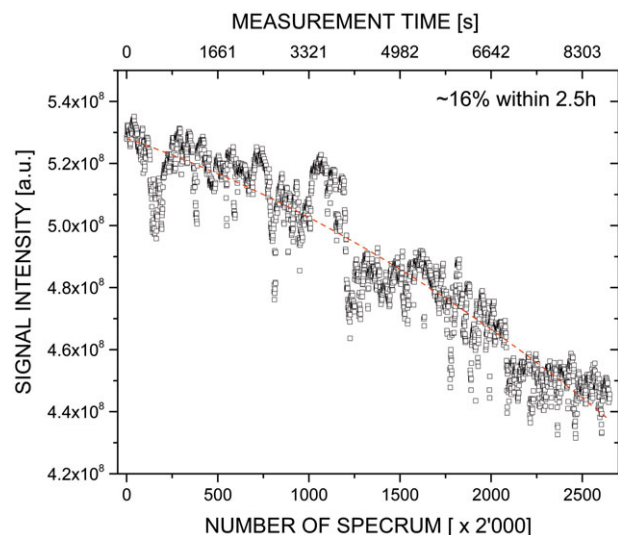


FIGURE 7 Intensity of the ^{40}Ar signal as a function of measurement time. In about 2.5 hours, approximately 16% of the gas is ionised and measured [Colour figure can be viewed at wileyonlinelibrary.com]

parameters of the linear regression used for the calibration. For the characterisation of the mass calibration accuracy, a mixture of Ar and Kr/Xe standard gases was measured. The left panel in Figure 8 displays the linear regression between the TOF of identified species and the square root of their mass to charge ratios. Since sufficient mass peaks were available, only singly charged species are used for calibration. The middle panel of Figure 8 depicts the mass residuals of ionised species used for calibration (the x-axis denotes the i th identified isotope/molecule peak). The residuals are defined as $(\text{Mass}_{\text{Calc}} - \text{Mass}_{\text{Lit}})$, where $\text{Mass}_{\text{Calc}}$ denotes the calculated mass of the identified isotope/molecule using the fit constants t_0 and k_0 and Mass_{Lit} the literature mass. Remember that heavier ionised species arrive later at the detector system. The right panel of Figure 8 shows a histogram of the mass residuals. There is Gaussian distribution and 50% of detected and identified peaks are within a mass calibration accuracy of about ± 100 ppm; about 87% of the peaks used for mass calibration have an accuracy of about ± 300 ppm or better. Note that the result is in good agreement with the estimation that the mass

calibration accuracy should be about 10 times larger than the instrumental mass resolving power (calibration accuracy is about $1/(10 \text{ times mass resolution})$). The EGT has a mass resolution ($m/\Delta m$) in the range 800 to 1200 (see Figures 4 and 5), which corresponds to an accuracy in the mass scale of approximately 100 ppm.

3.6 | Isotope ratio measurement accuracy

For the characterisation of the isotope ratio measurement accuracy of the EGT, we measured (1) the noble gases Kr and Xe from our calibration standards, (2) Hg within the background of the EGT, and (3) Ar laser extracted from a sample of the Millbillillie meteorite. The accuracy is defined as $(\text{IsoAbund}_{\text{Lit}} - \text{IsoAbund}_{\text{Meas}})/\text{IsoAbund}_{\text{Lit}}$, where $\text{IsoAbund}_{\text{Lit}}$ denotes the literature value of the isotope abundance and $\text{IsoAbund}_{\text{Meas}}$ the measured isotope abundance. For the Kr and Xe standard gas measurements and for the measurements of Ar from Millbillillie, the background signals were subtracted. In total, 10^6 spectra were recorded in each measurement, accumulated in 1000 files, each consisting 1000 single spectra. For the Hg background measurement, 2000 files each consisting 1000 spectra were recorded. For all three types of measurements, the number of recorded spectra could easily be increased because, the decrease of signal intensity over time is only moderate, and the background of Hg is very stable. With the increase of measurement time and hence the number of recorded spectra, the measurement accuracy can be increased with square root of recorded spectra. This is true until other factors dominate the measurement accuracy, such as electronic noise from the measurement card, background of residual gas, or accuracy of peak integration.

Figure 9 depicts recorded mass spectra (left panel) and the accuracy of the isotope ratios (right panel). For calculating the latter, we assume terrestrial values for Hg^{33} and we used the isotopic composition of the terrestrial atmosphere for Kr and Xe.¹⁴ All Kr isotopes could be detected during the measurement (Kr partial pressure $< 8.8 \times 10^{-13}$ mbar). Krypton-78, which has the lowest abundance of all Kr isotopes with a partial pressure of approximately 3×10^{-15} mbar, is slightly affected by the background noise (see insert) and is therefore not considered for isotope ratio analysis. The isotope ratios were measured with an accuracy of better than

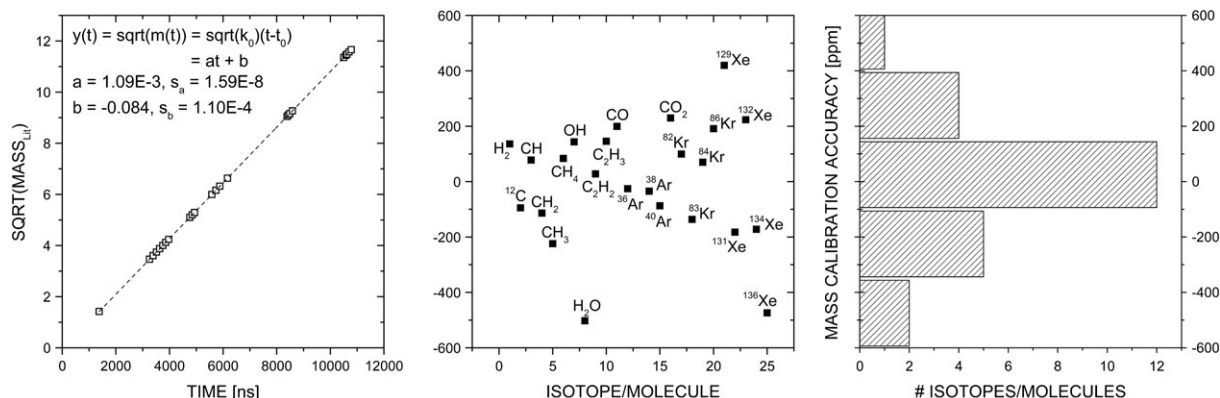


FIGURE 8 Mass calibration accuracy of the EGT. A linear regression of the square root of the mass as a function of the time-of-flight determines the fit parameter needed for mass calibration (left panel). Residuals of the mass calibration are shown in the middle panel, which are also shown as a histogram (right panel). The accuracy of the mass calibration is in the range ± 100 ppm

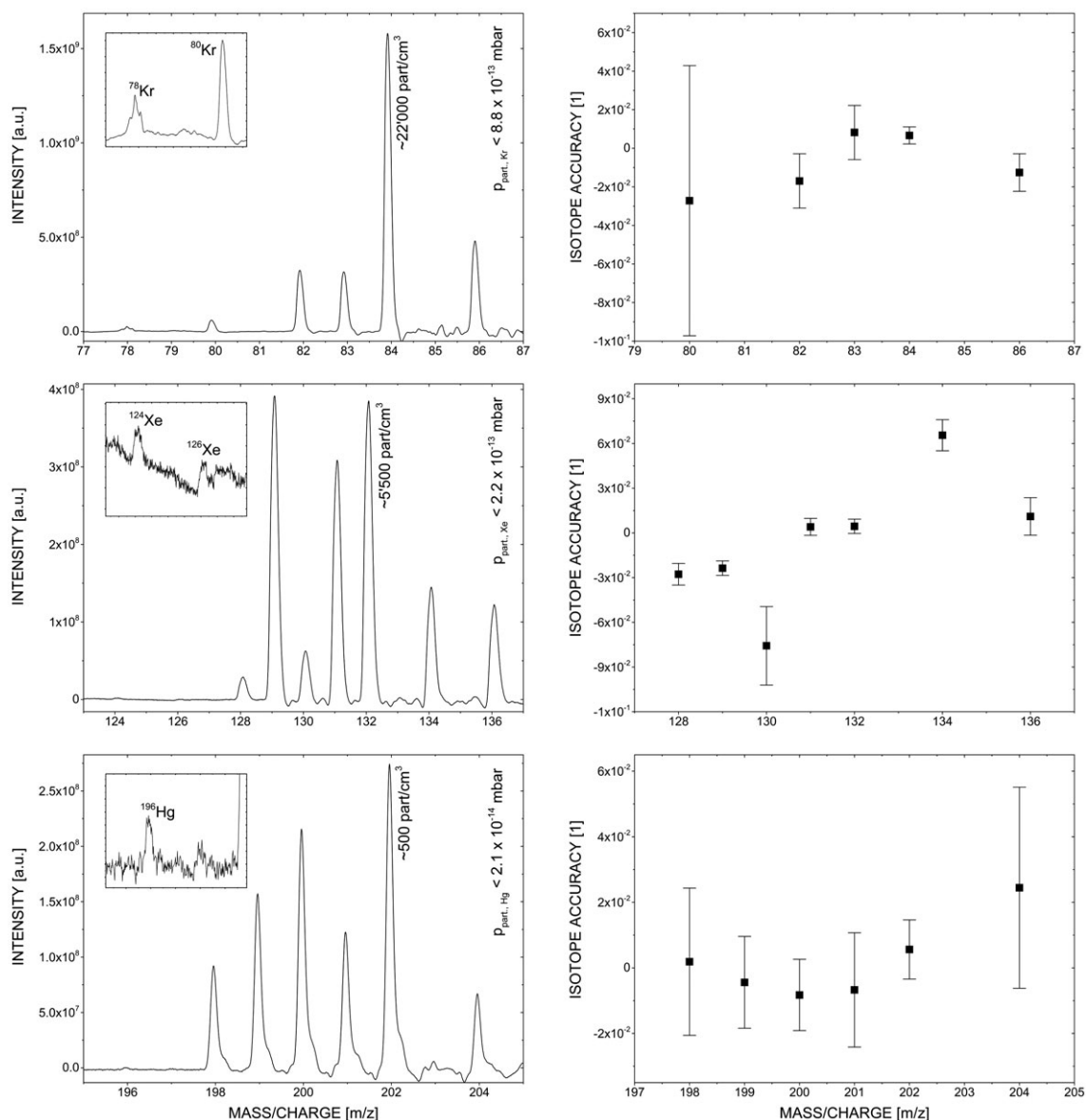


FIGURE 9 Mass spectra of Kr, Xe, and Hg isotopes (left row). Accuracy of isotope ratio analysis for the detected elements (right row). Best isotopic accuracy are typically observed for the major isotopes. Overall, best accuracies are observed for Hg. See text for more information

approximately 3%; the major isotope ^{84}Kr was measured with an accuracy of better than 7%. The result is slightly better for Xe isotopes. All Xe isotopes (Xe partial pressure of $< 2.2 \times 10^{-13}$ mbar) were detected and identified; even the Xe isotopes with the lowest abundance, ^{124}Xe and ^{126}Xe (at partial pressures of approximately 2×10^{-16} mbar). Since the peaks of ^{124}Xe and ^{126}Xe are affected by the baseline noise (see insert), they were both not considered for isotope ratio analysis. For the majority of the isotopes, an accuracy of better than approximately 3% is reached; the major isotopes ^{131}Xe and ^{132}Xe can be measured with an accuracy of approximately 4%.

All Hg isotopes could be detected with partial pressures $< 2.1 \times 10^{-14}$ mbar. However, for the lowest abundant isotope ^{196}Hg (partial pressure approximately 3×10^{-16} mbar), the signal-to-noise ratio is very low (see insert); this isotope is therefore not considered for the ratio analysis. For ^{204}Hg , which is second lowest in abundance, an accuracy of approximately 2.4% was measured. All other isotopes of Hg were detected with an accuracy at the per mill level. At a first

glance, it is surprising that Hg, which has the lowest partial pressure among all studied elements in this study, can be measured with the highest accuracy. The unexpected result is due to the background in the EGT (see Figure 3). There is a significant background at (m/z) values below approximately 150, which increases towards smaller (m/z) values and reaches a maximum at the level of (m/z) approximately 50. For Kr and Xe measurements, the background is significant and its subtraction compromises the accuracy of isotope ratio measurements. Consequently, reducing the background at lower (m/z) values will significantly increase the accuracy of the isotope ratio measurements for all noble gas species.

Figure 10 depicts the results of the Ar measurement for the Millbillillie meteorite. Note that we selected powders from the bulk meteorite and fully degassed this sample. Therefore, we cannot expect any spatial information concerning sampling depth and/or individual minerals or spots in the sample. All gas extracted during melting was collected and measured. The relevant isotopes ^{36}Ar and ^{38}Ar were

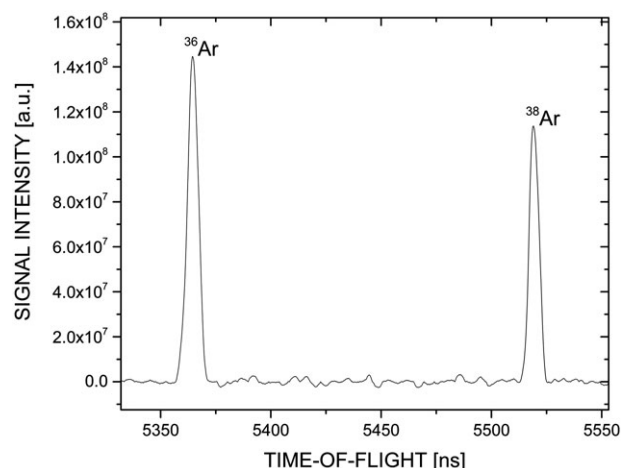


FIGURE 10 Argon measurement of the Millbillillie meteorite. Shown are ^{36}Ar and ^{38}Ar signals. The shown spectra is after blank correction

clearly detected and—as expected—their abundance significantly deviates from terrestrial values. Using results obtained earlier by us on the same meteorite but using sector field mass spectrometry, we can calculate that in this experiment, we have extracted approximately 10^9 atoms of ^{36}Ar from the approximately 3.5 mg of Millbillillie. For the extracted gas, we measured a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of approximately 1.6, which is well within the range of literature values (0.7–5.2).^{23,24,34}

4 | CONCLUSIONS

In this contribution, we present the measurement capabilities and figures of merit of a novel, compact reflectron-type TOF mass spectrometer for multielement isotope gas analysis. Measurements were conducted on Ar, Kr, and Xe standard gases, background gas within the instruments vacuum chamber showing trace amounts of Hg, and Ar extracted from the meteorite Millbillillie using a laser ablation set-up.

The measurements demonstrate that the instrument has a dynamic range of about six orders of magnitude, a mass resolving power ($m/\Delta m$) of up to approximately 1200 (measured at Hg, ^{16}O and CH_4 can be separated), and a high detection sensitivity, which allows the detection and identification of species at a partial pressure down to the low 10^{-16} mbar level. Single ion measurements showed that the in-house designed and built detector system (MCPs in synergy with an Apollonius anode) generates electric signals ranging from 20 mV to 200 mV per single ion event, corresponding to measured FWHM of detected peaks ranging from approximately 650 ps to approximately 1 ns, respectively. Measurements of single ion events showed fall times (bandwidth corrected) of better than 250 ps. The rise time could be shortened and the FWHM improved by integrating capacitors near the detection system.

Our isotope ratio measurements demonstrate that an accuracy at the per mill level can be reached. The best accuracy is reached for Hg, which is a contaminant and which has a partial pressure of $<2.1 \times 10^{-14}$ mbar. The minor isotopes of Kr and Xe were measured at the 2% to 3% level or better. The slightly lower accuracy at lower (m/z) values is due to the background correction; the background

significantly increases towards lower (m/z) values. Consequently, an improvement of the background at lower (m/z) values will significantly improve the accuracy of the isotope ratio measurements of the noble gases. Measurements of Ar extracted from the meteorite Millbillillie gave a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio of approximately 1.6, which agrees with literature values.

In summary, the EGT is a compact and sensitive multielement isotope gas analyser. The measurement performance of the EGT allows its operation in various scientific disciplines, ranging, eg, from the analysis of atmospheric gases to gases extracted from various types of solids. Especially in case limited and precious sample material is available only, the current figures of merit are of high interest as the system can provide the chemical composition (elements and isotopes) in a global context manner.

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ORCID

Andreas Riedo <http://orcid.org/0000-0001-9007-5791>

Surya Rout <http://orcid.org/0000-0003-0359-7693>

Reto Wiesendanger <http://orcid.org/0000-0001-7127-0516>

Peter Wurz <http://orcid.org/0000-0002-2603-1169>

Ingo Leya <http://orcid.org/0000-0002-3843-6681>

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