

**A QUANTITATIVE EVOLVED GAS ANALYSIS FOR METEORITES AND LUNAR SAMPLES.** A. B. Verchovsky, M. Anand and S. J. Barber, School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK, [sasha.verchovsky@open.ac.uk](mailto:sasha.verchovsky@open.ac.uk)

**Introduction:** Evolved gas analysis (EGA) consists of linear heating of a bulk-sample with the released gases continuously pumped through a mass spectrometer with registration of different masses. It allows identification of gases present in the sample and obtains their release patterns as a function of temperature. This method was successfully applied to Apollo lunar samples in the early 1970s [1, 2]. Different samples can be compared with each other in terms of the qualitative release patterns of different gas species. But quantitative comparison of the amount of gases present in different samples is not possible.

By developing Quantitative EGA (QEGA), we enable new insights into laboratory analyses of extraterrestrial samples. QEGA also informs the design and operation of spaceflight instruments being developed to perform analogous experiments *in situ* on the lunar surface such as within the European Space Agency's PROSPECT package [3]. The quantitative determination of volatiles within lunar regolith is also important for lunar *in situ* resource utilization (ISRU).

Quantitative EGA requires calibration of the measuring instrument (for example, quadrupole mass spectrometer) with reference gases, for which flow rate is determined independently in order to convert the signals from different gas species from samples into their flow rates, ultimately leading to their quantification and comparison with different samples.

**Experimental technique:** We used our custom-built Finesse mass-spectrometer system [4, 5], which contains a Hiden Analytical quadrupole mass spectrometer (QMS) equipped with an electron multiplier and evacuated by turbomolecular and ion pumps. The sample is wrapped in pure Pt foil and heated linearly within a furnace capable of reaching 1500 °C.

Several reference gases for calibration (single gas or gas mixtures) at 5-10 bar pressure were placed into a vessel connected to the vacuum system via a capillary leak or piezo-electric (PZT) metering valve. The (mostly viscous) flow rate was regulated either manually with a crimp (in the case of capillary) or automatically through software control of the voltage applied to the PZT valve. The flow rate was determined using a high sensitivity and precision MKS Baratron® capacitance manometer.

**Calibration procedures:** For calibration, we used pure gases or a gas mixture with 11 gas species (H<sub>2</sub>, He, CH<sub>4</sub>, Ne, N<sub>2</sub>, CO, O<sub>2</sub>, Ar, CO<sub>2</sub>, Kr and Xe with the following relative abundances: 56.78, 15.91, 1.452,

0.1011, 15.42, 1.03, 2.98, 1.002, 5.288, 0.02022, 0.01516 vol %, resp.) with well determined relative abundances (~1% rel.) resembling those observed in lunar soils. First, the gas flow rate was determined. For that, the reference gas was accumulated during a certain time in the volume of Baratron and the pressure was recorded after equilibration. The procedure was repeated several times with different accumulation time, which gives flow rate expressed in mbar/s. Subsequently, the reference gas was directed to the QMS and signals for a number of masses in the range from 2 to 132 (2, 4, 12, 14, 16, 18, 20, 22, 28, 29, 30, 32, 36, 40, 44, 84, and 132) were recorded in the continuous flow, using peak jumping mode and ion counting. For the same reference gas the procedure was repeated several times for different flow rates in the range from 10<sup>-8</sup> to 10<sup>-4</sup> mbar/s. Flow rate in mbar/s can be converted into ml/s, if the volume in which the gas is accumulated during Baratron measurement is determined. By integrating the release curves the gas concentrations in ml/g can be obtained.

**Calibration results:** Typical examples of flow rate calibration lines are presented in Figure 1.

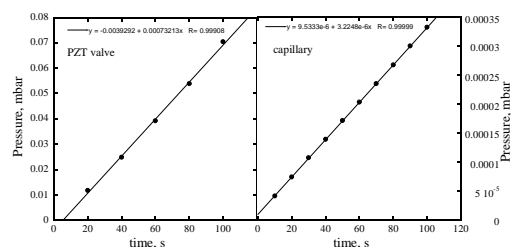


Figure. 1. Flow rate calibration for gas mixture using Baratron.

The dependence of the signal intensities at different masses on the gas flow rate are in general non-linear but can be well approximated by a power law (Fig. 2). Although the calibration gas mixture contains 15% of N<sub>2</sub> and 1% of CO, we do not see a contribution of CO on mass 28, since calibrations with pure N<sub>2</sub> and the gas mixture yield the same line within scatter of the experimental points. For this reason the mass 12 has been used for calibration of CO, since pure CO also gives signal at that mass, which is about only 30 times less than that at mass 28.

The use of pure gases for calibration enables the characterization of second order signals produced by some molecular gases as a result of their dissociation in

the QMS. The second order mass for  $N_2$  is 14, for CO is 12, for  $O_2$  is 16, and  $CO_2$  gives masses 28 and 16 in nearly equal amounts. Knowing the ratios between the main and second order signals for these gases allows us to calculate contribution of different gas species when they are present in a mixture and therefore, may contribute towards similar isobaric interferences, e.g. for  $N_2$ , CO and  $CO_2$  at mass 28.

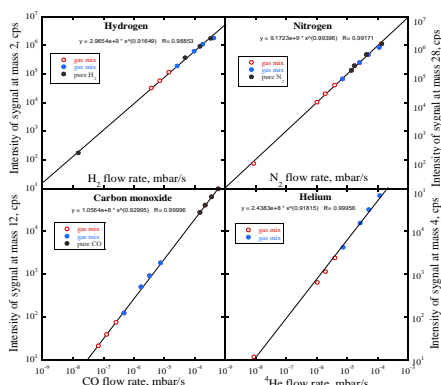


Figure 2. Representative QMS calibration curves for various gases.

We did not make calibration for water since it was challenging to achieve uniform heating of the vacuum line between the extraction furnace and the QMS to 100 °C. Therefore, some of the water extracted from the sample condensed in the pipe line, and thus, precluding its full quantification. However, we observed that calibration curves for different gases are very similar (Fig 2). The range of variation from average calibration coefficient is about  $\pm 30\%$ . We apply this average coefficient for estimation of water content.

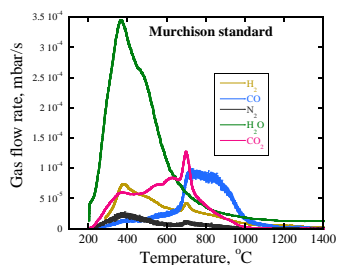


Figure 3. Release pattern of the major gas components from Murchison meteorite standard.

**Analysis of the PROSPECT reference Murchison meteorite sample:** As part of ESA's PROSPECT lunar exploration activity, a reference sample of Murchison (CM2) meteorite has been developed as a standard for volatile species investigations. A 3 mg powdered sample was heated at a rate of 6°/min from 200 to 1400 °C with recording of signals at 17 masses mentioned above, every second, such that about 10

scans were made at each temperature. A blank correction was applied through subtraction of the signal produced through a 'blank analysis' of an empty furnace.

The release pattern for each gas has been recalculated into flow rate variations using corresponding calibration curves (Fig. 3). As can be seen, water is the major component and this is only a lower limit for its amount since a part of it was condensed in the vacuum line between the furnace and the QMS. However, the release pattern of water seems not to be affected by its condensation in the pipes. Mass 28 is represented essentially by CO because it shows identical spectrum with mass 12. Therefore, for calculations of  $N_2$  amounts, we used signal at mass 14. Release pattern of  $CO_2$  is almost identical to that for mass 16, suggesting the presence of a small amount of methane. Mass 20 is almost exclusively associated with water ( $H_2^{18}O$ ). Among the minor components, we observe  $^4He$ , oxygen, Ar and Kr (Fig. 4).

Water, hydrogen and nitrogen are released mostly at lower temperatures (200-600 °C), whereas  $CO_2$  and especially CO are released at higher temperatures. For most gases, except for water and CO, a spike at  $\sim 700$  °C is observed reflecting probably chemical reactions or structural transformation of the heated material.

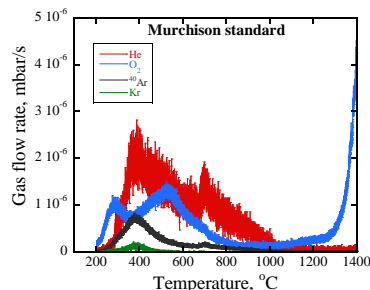


Figure 4. Release pattern of minor components from Murchison

**Conclusion:** For the first time a quantitative method for EGA has been developed and successfully applied for the analysis of Murchison meteorite. We plan to improve calibration of the system for water and apply the method for laboratory analyses of lunar samples. The method will also be implemented *in situ* on the Moon within the PROSPECT project.

**Acknowledgement:** This work was funded by UKSA (grant# ST/R001391/1 to MA and SB). PROSPECT is a program of and funded by ESA.

**References:** [1] Gibson E. K. Jr. and Jonson S. M. (1971) Proc. 2-nd LSC, 2, 1351-1366. [2] Gibson E. K. Jr. and Moor G. W. (1973) Proc. 3-d LSC, 2, 2029-2040. [3] Barber S. J, et al. (2018) VXIX LPSC, abstr. #2083. [4] Wright I P. et al. (1988) J. Phys. E 21, 865-875. [5] Verchovsky A. B. (2017) Geochem. Intern., 55, 957-970.