

A QUANTITATIVE EVOLVED GAS ANALYSIS FOR LUNAR AND METEORITIC MATERIALS. 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

Introduction: Evolved gas analysis (EGA) is a powerful tool widely used in different fields of research from investigations of chemical compounds in chemistry (polymers, complexes, catalysts, composite materials etc.) to technology (coating, food production, batteries etc.) to environment and Earth Sciences [1]. It consists of linear heating of a material with registration of the released volatile compounds by different methods such as gas chromatography, infrared spectroscopy and mass spectrometry (MS). The latter seems to be the most popular and effective method of volatiles registration since it provides a quick scan for a wide range of masses if quadrupole mass spectrometer (QMS) is used.

This method was successfully applied to Apollo lunar samples in the early 1970s [2, 3]. Gases from solar wind, inclusions and chemical reactions between different phases have been identified. Different lunar samples can be compared with each other in terms of the release patterns of different gas species. But quantitative comparison of the amount of gases present in different samples was 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 [4]. The quantitative determination of volatiles within lunar regolith is also important for *in situ* resource utilization (ISRU).

In this study we developed a QEGA just for QMS system without a carrier gas by calibration of the measuring instrument 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. The method has been applied for analyses of the Murchison reference sample and lunar soils.

Experimental technique: We used our custom-built Finesse mass-spectrometer system [5, 6], 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 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.

In addition we used a number of pure chemical compounds such as CaCO₃, NaHCO₃, CaC₂O₄*H₂O etc., which are decomposed according to their stoichiometry into gaseous components upon heating.

Calibration procedures: For calibration, we used pure gases or a gas mixture with 11 gas species (H₂, He, CH₄, Ne, N₂, CO, O₂, Ar, CO₂, 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 10⁻⁸ to 10⁻⁴ 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 then be obtained.

For calibration with chemical compounds we used the same heating rate as for the sample. In this case direct comparison of the areas under corresponding peaks for the reference material and sample gives concentration of gases.

Calibration results: 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 N₂ and 1% of CO, we do not see a contribution of CO on mass 28, since calibrations with pure N₂ 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 strong compared to 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.

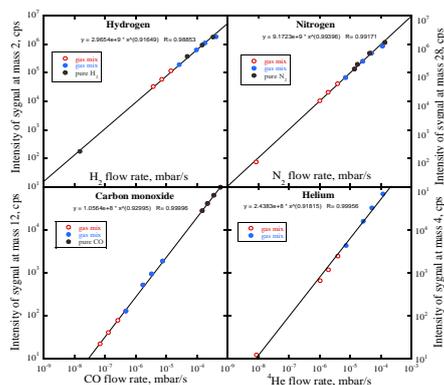


Figure 1. Representative QMS calibration curves for various gases.

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 $6^\circ/\text{min}$ from 200 to 1400 $^\circ\text{C}$ 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.

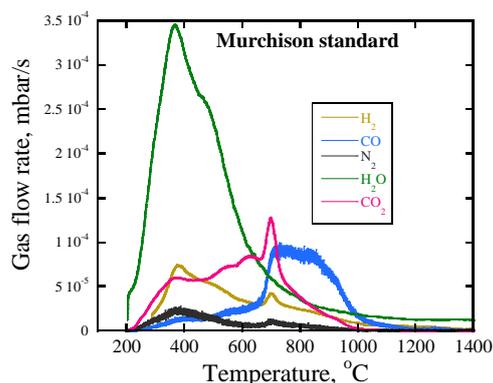


Figure 2. Release pattern of the major gas components from Murchison meteorite standard.

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 $^\circ\text{C}$), whereas CO_2 and especially CO are released at higher temperatures. For most gases, except for water and CO, a spike at $\sim 700^\circ\text{C}$ is observed reflecting probably chemical reactions or structural transformation of the heated material.

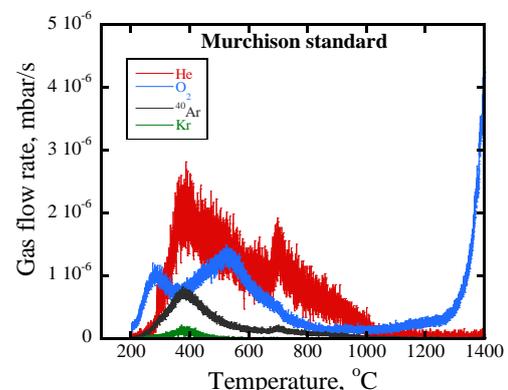


Figure 3. Release pattern of minor components from Murchison

The results for gas concentrations in ml/g in the Murchison standard obtained by EGA and their comparison with those obtained by combustion [7] will be presented at the conference.

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 the analyses of lunar samples. The method will also be implemented *in situ* on the Moon within the PROSPECT project.

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References: [1] Risoluti R and Materazzi S. (2018) *Applied Spectroscopy Reviews*, 1-29. [2] Gibson E. K. Jr. and Jonson S. M. (1971) *Proc. 2-nd LSC*, 2, 1351-1366. [3] Gibson E. K. Jr. and Moor G. W. (1973) *Proc. 3-d LSC*, 2, 2029-2040. [4] Barber S. J, et al. (2018) *VXIX LPSC*, abstr. #2083. [5] Wright I P. et al. (1988) *J. Phys. E* 21, 865-875. [6] Verchovskiy A. B. (2017) *Geochem. Intern.* 55, 957-970. [7] Mortimer J. et al. (2017) *ELS*, abstr.