A QUANTITATIVE EVOLVED GAS ANALYSIS FOR EXTRA-TERRESTRIAL SAMPLES.

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Abstract

Evolved gas analysis (EGA) has been successfully applied to the studies of meteorites and Apollo lunar samples. It consists of linear heating of a material with registration of the released volatile compounds, typically using a spectrometric technique. However, so far no quantitative comparison was possible of the amount of gases released during heating of a sample. To address this limitation, we have developed a Quantitative EGA (QEGA) technique using our custom-built Finesse mass spectrometry system. It is based on calibration of the quadrupole mass spectrometer with reference gases (e.g. CO\textsubscript{2}, CO, H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2} or their mixtures with known relative abundances) with known flow rate. The method was tested using simple chemical compounds such as CaCO\textsubscript{3}, which give well-known amounts of pure gases during their thermal decomposition. We present initial QEGA data on two reference meteorites, Allende and Murchison. Our QEGA work is also informing the design and operation of ProSPA spaceflight instruments being developed to perform analogous experiments \textit{in situ} on the lunar surface through the European Space Agency’s PROSPECT payload on Luna 27.

Keywords: Evolved Gas Analysis; Volatiles; Meteorites; Allende; Murchison

Declaration of interest: Drs Sheridan and Morgan are employees of The Open University and are founders/directors of Applied Science & Technology Solutions Ltd, that has a Manufacturing License Agreement with The Open University to commercialise the patented PZT valve. They are both named inventors on the OU patent. The valves used in this study were manufactured at The Open University.

1. Introduction

Evolved gas analysis (EGA) is a powerful tool widely used in different research applications from investigations of chemical compounds in chemistry (polymers, complexes, catalysts, composite materials etc.) and technology (coating, food production, batteries etc.) to environment and Earth Sciences (see Risoluti and Materazzi, 2018 and references therein). 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 universal and effective method of volatiles registration, and if a quadrupole mass spectrometer (QMS) is used, it enables rapid identification of a wide range of evolved
gases through the characteristic mass-to-charge ratio (m/z) of their fragment ions. Often the EGA is used in combination with thermoanalysis (TA) or thermogravimetric analysis (TGA). TA-MS EGA allows identification of temperature effects during heating of materials as a result of their structural transformations while TGA-MS EGA additionally records mass loss. Thus TGA-MS gives a possibility not only to identify released gases, obtain their release patterns as a function of temperature and establish corresponding mass loss but also to associate them with mechanisms of their release such as chemical reactions or structural transformation occurring in the heated materials.

Investigations of gases in rocks have always been an important theme in geology starting from pioneering works at the beginning of the twentieth century (Chamberlin, 1909) and continuing through to investigations of Martian rocks by the Curiosity rover (Ming et al., 2014). EGA applied to Earth Sciences aims primarily to identify gases trapped within rocks or minerals in order to characterise fluid environment during their formation or later transformations such as metamorphism or metasomatism. An interesting application for terrestrial samples is a combination of EGA with continuous crushing (Xiao et al., 2019), which allows separation of gases trapped in fluid inclusions from those released from the lattice. For extra-terrestrial materials, especially in case of lunar samples, the solar wind implanted gases are also of interest. EGA was successfully applied to Apollo lunar samples in the early 1970s (Gibson et al., 1971, 1972). Gases from implanted solar wind (H\textsubscript{2}, He) and inclusions (CO, CO\textsubscript{2}, N\textsubscript{2}) together with gases (CO) released as a result of chemical reactions among minerals have been identified. Different lunar samples can be compared with each other in terms of the release patterns of different gas species. However, a quantitative comparison of the amount of gases present in different samples has not been previously achieved. In these previous studies, it also was not possible to compare the relative amounts of gases released by a single sample either, as often the release profile at each m/z ratio was normalised to its maximal value.

This work, therefore, aims at developing Quantitative EGA (QEGA), in order to enable new insights into laboratory analyses of extra-terrestrial samples. In addition, QEGA would inform 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 (Barber et al., 2018). The quantitative determination of volatiles within lunar regolith is also important for lunar in situ resource utilization (ISRU) (Anand et al., 2012).

Several authors have previously reported on attempts to develop QEGA for TA-MS and TGA-MS systems which use a carrier gas (Maciejewski and Baiker, 1997; Xia and Wei, 2015). This requires calibration of QMS
sensitivity for different gases and flow rate of the carrier gas. For calibration, pure gases as well as compounds
with well-known decomposition stoichiometry (e.g. NaHCO$_3$) were used.

In this study we developed a QEGA just for the QMS system without a carrier gas by calibration of the
measuring instrument with reference gases, for which the 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 allowing comparison with different samples. The method has been applied for analyses of
Murchison and Allende reference samples, prepared in the context of ESA’s PROSPECT activity (Mortimer et
al., 2017).

2. Experimental set up and measurement procedures

The experimental setup is shown in Fig. 1. It is a part of our Finesse mass spectrometric system for multi-
element analyses (Verchovsky, 2017). Reference gas from a high-pressure (up to 200 bars) cylinder was placed
into pre-evacuated reference gas vessel (~0.5 l) via valves 1 and 2, at 4-10 bar pressure, as measured with a
mechanical pressure gauge. Valve 2 was kept open, to monitor the pressure stability throughout the calibration
process. The MKS Baratron® capacitance manometer provides a 10 volt output at its 1 torr upper limit with a
resolution of 0.01 mV thus giving 6 orders of magnitude dynamic range for flow rate measurements of reference
gases. The flow rate was regulated with a piezo-electrically actuated (lead zirconate titanate or ‘PZT’) metering
valve (Sheridan et al., 2010) which provides a variable flow restriction as a function of an applied regulating
voltage in the range 0-100 V. The PZT valve provides an analogous functionality to a standard capillary with
crimp (Sheridan et al., 2010), providing an acceptably stable flow rate at a given operating voltage (see sect.
3.1). The flow rate of a reference gas is determined by its accumulation in the volume between PZT valve and
Baratron® for a certain amount of time when valves 4, 7 and 12 are open and valves 3, 5, 6, 8, 9 and 10 are
closed and the PZT valve is opened at a constant voltage. Then valve 4 is closed and the Baratron® pressure (in
mbar) is recorded after 20 second of gas equilibration time. Afterwards, the gas is pumped away with turbo and
ion pumps via valves 5 and 9, respectively and the procedure is repeated several times for different
accumulation time with unchanged PZT valve voltage. This procedure yields flow rate in mbar/s. In order to
express the flow rate in cc/s the volume from PZT valve to Baratron® was determined by putting helium in this
volume at a certain pressure (Po); after equilibration with the volume-calibrated container (Vc) the pressure P1
is recorded while V6 is opened. The volume where the gas was accumulated during flow rate determination is
found as:
\[ P_1^*Vc/(P_0-P_1) \].

Figure 1. Schematic of the experimental setup

Directly after the flow rate calibration the reference gas was directed to the QMS via valves 4, 7 and 10 with valves 3, 5, 6, 8, 9 and 12 closed keeping PZT voltage the same and the signals for a number of masses in the range from 2 to 132 were recorded in the continuous flow pumping gas through QMS via valve 11 to turbo and ion pumps working in parallel. The signals were registered 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.

Following calibration, EGA was performed by putting a sample (wrapped in platinum foil) into the extraction furnace and subjected to linear heating in the range from 100 to 1400 °C. The released gases were continuously pumped through QMS via valves 8, 10 and 11 (with valves 7, 9 and 12 closed) with registration of the same masses as during calibration. Additionally, blank experiments were performed using empty Pt foils.

During QMS measurements we monitored pressure measured by the ion pump controller. These measurements are not particularly precise, nevertheless, correlation between the pressure and flow rate is relatively good (Fig. 2). This gives us an opportunity to use this pressure as an independent indication of gas release during sample analyses.
We note that the system was not particularly designed for water analysis, since the pipes between the extraction furnace and QMS were not heated to 100 °C in order to prevent water condensation.

All the procedures described above, apart from filling the reference vessel with a reference gas, are fully automated and controlled by a computer. All valves, except 1 and 2 are pneumatically activated, controlled by solenoid valves, which in turn are controlled via optically isolated digital output NI1705 card. The Baratron output was connected to a Keithley digital voltmeter, and as the voltage source for PZT valve, we used Keithley 6487 Picoammeter/Voltage source both controlled via serial ports.

Figure 2. Correlation between flow rate and pressure measured on ion pump for different gas mixtures. Note that the pressure measured by the ion pump is gas specific, for which reason the lines for different gas mixtures are not coincident with each other.

3. Results

3.1. Flow rate calibration

For the flow rate calibration, we used pure gases such as CO₂, CO, O₂, H₂, N₂, CH₄, two artificial gas mixtures, containing 11 common gases with the relative abundances (resembling those of lunar soils) shown in Table 1 and a mixture with atmospheric composition. The mixtures were prepared by Air Products with precision for relative abundances of the individual species better than 2 per cent and were stored into 50 L cylinders with 200 and 12 bar pressure for Mixtures 1 and 2, respectively. A standard 200 L cylinder with compressed air at 80 bar pressure was used as a reference gas mixture with atmospheric composition.
For this calibration, accumulation times from 10 to 100 s with 10-20 s increment were used. Typical calibration lines are shown in Figure 3. The slopes of the lines give flow rate in mbar/s, that can be converted into cc/s as stated above. Precision of the slopes is within 1-2% (1σ).

Figure 3. Examples of flow rate calibration. Errors on slopes are shown for the corresponding final two or three digits.

3.2. QMS sensitivity calibration

During continuous pumping of a reference gas with known flow rate through QMS (after pressure is stabilised) the intensities of 10-20 masses in the range from 2 to 132 (m/z=2, 3, 4, 12, 14, 16, 17, 18, 20, 22, 27, 28, 29, 30, 32, 36, 39, 40, 44, 84, 132) were recorded during 200 scans using peak jumping mode with 20 ms integration time. The procedure was repeated 3 times with 5 min pumping time between measurements. The
dependence of peak intensities on flow rate represents QMS sensitivity with respect to different species. The best fit for the experimental points in the wide range (several orders of magnitude) of QMS signals and flow rates approximates to a power law (Fig. 4). The QMS sensitivity is expressed as cps/(mbar/s) or cps/(cc/s) and depends on flow rate. It is important to note here that pure gases and gas mixture give indistinguishable calibration curves over the range of a few orders of magnitude, indicating that no significant element fractionation occurs during transition of a gas between the reference gas container and QMS, since flow rates of individual gases in the gas mixtures were found using the relative abundances of the gases from the Table 1.

![Figure 4. QMS sensitivity calibration.](image)

However, the measured elemental ratios vary depending on flow rates (Fig. 5). The reason for this element fractionation could be twofold: it can occur in the PZT valve during transition of gas to QMS and/or in the ion source of QMS. Since the PZT valve works the same way as a capillary, element fractionation in it is determined by the flow regime. With increasing flow rate/capillary diameter the heavy elements/isotopes show enrichment compared to the lighter ones under a molecular flow regime. The sensitivity of QMS with respect to different gas species is different due to variations in their ionisation potential. Additional fractionation can be a result of mass discrimination in the ion source depending on pressure. These are complicated processes, especially for chemically reactive gases, which can change the measured elemental ratios in the same direction.
as it happens during mass fractionation in the PZT valve. As a result, it is difficult to distinguish between the two processes.

Figure 5. Element fractionation in QMS depending on flow rate.

The experimental data (Fig. 5) show that for chemically reactive gases the element ratios vary by a factor of 1.3-2 (depending on flow rate) to the direction expected under a molecular flow regime. On the other hand, for chemically inert noble gases the variations are much smaller (almost negligible), though the relative differences in masses for the former and the latter are similar. This suggests that the reason for fractionation is variations in the relative sensitivity of QMS with respect to different chemically reactive gases depending on their pressure, rather than fractionation in the PZT valve. The latter seems to provide mostly a viscous flow at 4-5 bar pressure in the reference gas container that follows from almost no element fractionation for noble gases. In addition, as it was mentioned above, if the variations of the elemental ratios (up to factor of 2) for chemically reactive gases were caused by fractionation in the PZT valve, the data points on the calibration plots (Fig. 4) for pure gases and gas mixtures would not make single calibration lines.

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 (\(^{14}\text{N}^+\)), for CO is 12 (\(^{12}\text{C}^+\)), for O$_2$ is 16 (\(^{16}\text{O}^+\)), CO$_2$ gives masses 28 (\(^{12}\text{C}^{16}\text{O}^+\)) and 16 (\(^{16}\text{O}^+\)) in nearly equal amounts and CH$_4$ gives mass 2 (H$^+$) (Fig. 6). The ratios between signals for the main and second order masses are in agreement with observations made earlier (Hourlier, 2018), though the ratios depend on the QMS settings and flow rates.

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 $\text{N}_2$, CO and CO$_2$ at mass 28. When using a mixture of gases for calibration in some cases it is better to use a second order signal instead of the main where interference is expected. For instance, for CO calibration we used mass 12 instead of 28, which is mostly made of $\text{N}_2$ for our gas mixture, and obtained a good calibration line including data for the gas mixture and pure CO (Fig. 4).

![Figure 6. The main and the second order signals for pure gases.](image)

It is important that calibration and sample analyses are made with the same QMS sensitivity. To control the QMS sensitivity calibration should be repeated before and after each sample analysis.

### 3.3. Testing the method with pure chemical compounds

For this purpose we used solid samples such as CaCO$_3$ (NBS 18 standard), CaC$_2$H$_4$*H$_2$O, NaHCO$_3$ and PdO (all from Fisher Scientific with more than 99% purity), which yield known (stoichiometric) amounts of gases (CO, CO$_2$, O$_2$) during their thermal decomposition. Before and after each decomposition experiment we ran calibration using pure gases, CO, CO$_2$, or O$_2$ and calculated amounts of the released gases using both calibrations, which were in a good agreement with each other.

To calculate absolute amounts of the released gases we first translate corresponding signals in cps to cc/s...
using calibration line. Since the experimental points are fitted with a power law in the form:

\[ \text{signal int. (cps)} = a \times (\text{flow rate (cc/s)})^b, \]

where \(a\) and \(b\) – the fitting parameters, the translation coefficient \((k)\) is expressed as:

\[ k = 10^{\frac{\log(\text{signal int.}) - \log(a)}{b}}. \]

The amounts of gases released were calculated by integrating the release curve (in cc/s) over time as, for example, shown in Figure 8. Obviously, the integration cannot be made analytically. Therefore, to determine the area under the release curve we used “weighing method”, consisting of printing the plot on a sheet of paper and cutting it along the axes. Then, the weight of the whole plot area was determined using a precision balance. Next, the area under the curve was cut and weighed. The amount of the released gas is then given by

\[ \frac{\Box x \times \Box y}{\Box x \times \Box y} \times (\text{weight of the area under the curve} / \text{weight of the area of the whole plot}), \]

where \(\Box x\) and \(\Box y\) – are the lengths of the plot along the axis in corresponding units. Verification of the method using a simple function that can be integrated analytically, for instance \(y = x^2\), gives an error about 1-2%.

3.3.1. Calcium carbonate

We analysed 5 different aliquots of pure CaCO\(_3\). Thermal decomposition of CaCO\(_3\) gives only CO\(_2\) in the temperature range 550-750°C. In most of the analyses mass 44 was too high to measure since the signal oversaturated the secondary electron multiplier and tended to level off at \(\sim 2 \times 10^6\) cps due to multiplier dead time (~10\(^{-6}\) s). The problem with the saturation is caused by the necessity to find a compromise between QMS sensitivity (in order to have good signals not only on the main but on the second order masses as well), the sample size (to have a reasonable sample weighing error) and the reference gas flow rate (to avoid overpressure in the QMS ion source). In this case, if possible, we used the second order signals at mass 12, 16 or 28, which are significantly smaller than that at mass 44 (see Fig. 6) with calibration at corresponding masses. Otherwise, if the second order masses were too small to provide reasonably precise calculations, only a low limit of CO\(_2\) concentrations can be estimated using the signal at the main mass, if the latter is saturated.

An example of the release pattern of CO\(_2\) during thermal decomposition of CaCO\(_3\) is show in Figure 7. Maximum release is observed at 680°C in good agreement with known decomposition temperature of CaCO\(_3\).
The signal at mass 44 is slightly cut off at maximum release due to the multiplier saturation effect. The mass 28 has an additional peak at 800°C; however, as there is no corresponding peak at mass 44, this is unlikely to be CO₂, but could be CO or nitrogen.

Figure 7. Kinetics of CaCO₃ decomposition during linear heating with 6°/min recorded at different masses. Variations in the total pressure measured at QMS are also shown. Numbers next to curves indicate m/z.

In order to calculate the amount of CO₂ released we plotted the flow rate of CO₂ release (in cc/s) versus time (Fig. 8). In this example we determined the area under the curve for mass 16 compared to the area of the whole plot to be 0.170. The amount of CO₂ released is then determined as 5x10⁻⁵ cc/s * 4000 s * 0.170 = 0.330 cc.

Figure 8. Release of CO₂ from CaCO₃ versus time at 6°/min for masses 16 and 28.

The kinetics of CaCO₃ decomposition depends on heating rate: at a higher heating rate the release peak is broader with a maximum at a slightly higher temperature than at a lower heating rate (Fig. 9). But in general the decomposition temperature, 700±20°C, corresponds well to that known for CaCO₃.
Figure 9. Decomposition of CaCO$_3$ as recorded at mass 16 at different heating rates.

The results of all analyses of CaCO$_3$ are listed in Table 2. There are no systematic differences between true and calculated amounts depending on heating rate and masses used for calculations: the average deviation of all calculated CO$_2$ amounts from the theoretical ones is -0.14±23% (1σ).

Table 2. The theoretical and calculated amounts of CO$_2$ released during thermal decomposition of CaCO$_3$.

<table>
<thead>
<tr>
<th>Sample mass, mg</th>
<th>Theoretical CO$_2$ content, cc</th>
<th>Heating rate, °C/min</th>
<th>Calculated amounts of CO$_2$ for different masses</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.133</td>
<td>0.0298</td>
<td>6</td>
<td>Mass 12: 0.0251, Mass 16: 0.0328, Mass 28: 0.0329, Mass 44: &gt;0.0198</td>
</tr>
<tr>
<td>0.093</td>
<td>0.0208</td>
<td>20</td>
<td>n.a.: 0.00165, 0.0189: n.a.</td>
</tr>
<tr>
<td>0.109</td>
<td>0.0244</td>
<td>20</td>
<td>n.a.: 0.0191, 0.0172: n.a.</td>
</tr>
<tr>
<td>0.057</td>
<td>0.0128</td>
<td>20</td>
<td>0.0139, 0.0158: 0.0082: n.a.</td>
</tr>
<tr>
<td>0.074</td>
<td>0.0166</td>
<td>10</td>
<td>0.0202, 0.0191: 0.0245, 0.0158</td>
</tr>
</tbody>
</table>

3.3.2. Calcium oxalate monohydrate

Thermal decomposition of CaC$_2$O$_4$·H$_2$O produces water, carbon monoxide and carbon dioxide at 200, 500 and 600-700 °C respectively. Here we consider only release of CO and CO$_2$, since our system was not designed for water analysis. In the major gas peak at 500 °C most of CO and ~25% of CO$_2$ are released. The higher temperature gas release at 650 °C accounts for most of CO$_2$ and about 20% of CO (Fig. 10).
Figure 10. Thermal decomposition of CaC$_2$O$_4$·H$_2$O at 12°/min heating rate. a) –the major peaks (masses 28 and 44) and the total pressure; b) – the second order peaks (masses 12 and 16).

Pure CO$_2$ and CO reference gases were used for calibration run before and after each sample. For calculations of the amounts of CO$_2$ we used both the main and the second order signals, i.e. at mass 16 and 44 for CO$_2$, and for CO – only mass 28, since signal at mass 12 has a significant contribution from CO$_2$. The results for calcium oxalate monohydrate are summarised in the Table 3.

Table 3. The theoretical and calculated amounts of CO and CO$_2$ released during thermal decomposition of CaC$_2$O$_4$·H$_2$O.

<table>
<thead>
<tr>
<th>Sample mass, mg</th>
<th>Theoretical CO$_2$ content, cc</th>
<th>Theoretical CO content, cc</th>
<th>Heating rate, °/min</th>
<th>Calculated amounts of CO$_2$ for different masses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mass 28</td>
</tr>
<tr>
<td>0.063</td>
<td>0.0096</td>
<td>0.0096</td>
<td>20</td>
<td>&gt;0.0062</td>
</tr>
<tr>
<td>0.042</td>
<td>0.0064</td>
<td>0.0064</td>
<td>20</td>
<td>&gt;0.0033</td>
</tr>
<tr>
<td>0.047</td>
<td>0.0072</td>
<td>0.0072</td>
<td>20</td>
<td>&gt;0.0040</td>
</tr>
<tr>
<td>0.067</td>
<td>0.00102</td>
<td>0.00103</td>
<td>12</td>
<td>0.0084</td>
</tr>
<tr>
<td>0.056</td>
<td>0.0086</td>
<td>0.0086</td>
<td>12</td>
<td>0.0081</td>
</tr>
</tbody>
</table>

The average value and standard deviation of the calculated values from the theoretical one is 3±17%, basically similar to the result obtained for CaCO$_3$.

3.3.3. Palladium oxide
Thermal decomposition of PdO yields 13.1 wt % oxygen at about 650 °C (Fig. 11). The second order signal is observed at mass 16. The main signal at mass 32 was in all measurements (3 samples) too high to provide accurate calculations.

Figure 11. Thermal decomposition of PdO at 12°/min heating rate. Numbers next to curves indicate m/z.

The deviations of the calculated amounts of O₂ from the theoretical ones (Table 4) in the samples analysed show similar scatter as was observed for other compounds (see sections 3.3.1 and 3.3.2.).

Table 4. The theoretical and calculated amounts of O₂ released during thermal decomposition of PdO.

<table>
<thead>
<tr>
<th>Sample mass, mg</th>
<th>Theoretical O₂ content, cc</th>
<th>Heating rate, °/min</th>
<th>Calculated amounts of O₂ for different masses, cc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mass 16</td>
<td>Mass 32</td>
</tr>
<tr>
<td>0.077</td>
<td>0.0071</td>
<td>20</td>
<td>0.0086 &gt;0.0040</td>
</tr>
<tr>
<td>0.196</td>
<td>0.018</td>
<td>12</td>
<td>0.025 &gt;0.069</td>
</tr>
<tr>
<td>0.106</td>
<td>0.0097</td>
<td>12</td>
<td>0.0082 &gt;0.051</td>
</tr>
</tbody>
</table>

3.3.4. Sodium bicarbonate

Thermal decomposition of NaHCO₃ occurs at about 170°C with formation of H₂O and CO₂ (Fig. 12).
Figure 12. Thermal decomposition of NaHCO$_3$ at 12°/min heating rate. Numbers next to curves indicate m/z.

The signals at masses 44 and 18 were saturated, therefore, to quantify the amounts of CO$_2$ and water we used the second order signal at mass 28 and 17 respectively. It gives 0.026 cc of CO$_2$ versus 0.022 cc expected from the 0.164 mg sample aliquot used in the decomposition experiment. The difference is within the same range of uncertainty as observed for other decomposition experiments (see above).

The clear release peak of H$_2$O from the sample suggests that water can be registered in spite of its condensation in the pipes between the extraction furnace and QMS. This result is used to calibrate the QMS for water. For that we calculated the integral of mass 17 signal over time that consists of 1.24x10$^6$ cps, which corresponds to the 1.75x10$^{-3}$ g of water in the sodium bicarbonate sample analysed. Thus, we found the QMS sensitivity factor for water to be 1.41x10$^{-13}$ g/cps, which we used for evaluation of water content in the meteorite samples (see section 5) suggesting that condensation process for the reference and meteorite samples occurs in a similar way.

4. Analysis of errors associated with QMS calibration

The plot in Figure 13 summarises the result for all chemical compounds analysed. As can be seen, the distribution of the relative deviations of the measured amounts from those calculated for the compounds is almost symmetrical with median value close to zero pointing to a good accuracy of the measurements. The standard deviation of the distribution is 22%.

![Figure 13. Distribution of the relative deviations between measured and true concentrations of gases for chemical compounds analysed.](image)

Since the flow rate calibration curves represent a power function and the sample gas flow rate is calculated in the form of $10^{(\log(x)-\log(a))/b}$, where $x$ is the measured sample signal and $a$ and $b$ are calibration curve fitting parameters.
parameters, the errors of a and b are very critical for the error of the flow rate. For a typical calibration curve shown in Figure 14a the errors for a and b can be found if x and y are replaced by their logarithms (Fig. 14b). The calibration line is transformed into a straight line for which errors of intercept and slope can be calculated using square root method. For the given example the expression for flow rate is 
\[ x = 10^{(\log y - 13.973\pm0.406)/(2.5883\pm0.0960)} \],
where y is the signal at mass 12 measured during decomposition of the CaCO\(_3\) sample.

We used the error propagation calculator (www.colby.edu/chemistry/PChem/scripts/error.html?ModPagespeed=off) to calculate error of the above expression, which consists ~45% of the x (flow rate) value. Similar relative error is obtained for the amount of CO\(_2\) released after integration of the release curve (Fig. 14c). The results presented in the tables 2-4 show somewhat lower errors than estimated mostly because we used several calculations for the same sample that should reduce the uncertainty. In order to reduce the error for the amount of gas to ~15% the errors for the slope and intercept of the calibration line should be reduced from actual 3-4% to ~1%. This seems to be achievable if the major signals are measured on Faraday cap and the minor – on multiplier. Our model of QMS does not however allow this.

Figure 14. Error propagation for the calculated amounts of the released CO\(_2\). a) – calibration curve in linear scale, b) – calibration curve in logarithmic scale with errors, c) – release of CO\(_2\) with error bars (shadow area).

5. Analyses of the standard meteorite samples Murchison and Allende

As part of ESA’s PROSPECT lunar exploration activity, two reference samples of Murchison (CM2) and Allende (CV3) meteorites have been developed as standards for volatile species investigations (Mortimer et al., 2017). Isotopic compositions and concentrations of C, N and some noble gases have been analysed in these two samples using different methods. Below we explain how the EGA of the samples can be explained and
quantified on the basis of the calibration procedures discussed above.

Figure 15. Release patterns of different gas species (b-d) and pressure variations (a) during EGA of the Allende meteorite standard with heating rate 12 °C/min. Numbers next to curves indicate m/z.

5.1. Allende

A 3.29 mg sample was used for the QEGA. As can be seen from Figure 15a, there are three major peaks of pressure which coincide with the peaks of QMS signals at masses 44 and 28 (Fig 15b). The first low temperature peak is represented mostly by mass 44 with much smaller but similar shaped peaks at masses 16 and 28. This is a good indication that the low-temperature peak is made predominantly of CO$_2$. The major contribution for the middle- and high-temperature peaks is from mass 28. At the same time, the peaks at mass 44 and 16 are significantly lower in this temperature range. This represents clear indication that the middle- and high-temperature peaks correspond to release of CO. If there is a contribution from nitrogen on these peaks, it must be very low, since no signal at mass 14 is observed.

Using calibration with pure CO$_2$ gas we calculated the amounts of C released at low and high temperature range. For the low temperature peak of CO$_2$ (200-600 °C) we used the signal at mass 44 and obtained 0.14±0.04% of the total C in the sample. For the high-temperature release of CO the signal at mass 28 has been used that gives 0.20±0.05% of the total C in the sample. So, the total calculated C concentration in the sample is 0.34±0.07% vs. 0.4±0.1% obtained by another independent methods (Mortimer et al., 2017). Taking into
account all associated uncertainties with the QEGA measurements and data reduction (~30%), there is a
reasonable agreement between the two methods.

Release of SO$_2$ is clearly indicated by signal at mass 64 (Fig. 15d). There are two low- and high-
temperature releases of the gas associated with decomposition of different sulphur compounds such as troilite
and pentlandite and oxidation of sulphur as a result of chemical reactions with oxygen containing minerals.
Notably the high-temperature release of SO$_2$ does not coincide with the release of pure oxygen at the very high
temperature. The latter appears to be a result of decomposition of SiO$_2$ vapours produced by the hot quartz of
the extraction furnace sample tube at T >1300 °C that coincides with significant increase of pressure. Pt foil
used to wrap the samples acted as a catalyst for the process. Apparently, this oxygen does not play an important
role in the production of SO$_2$. Hydrogen release is broad (Fig 15c) and seems to be associated mainly with
decomposition of organic compounds. Calculation of the hydrogen absolute amount using calibration with gas
mixture 2, containing 57 vol. % of hydrogen (Table 1) gives 0.01 wt. % H, which is close to the values
determined by other methods, 0.006 wt. % (Kerridge, 1985; Alexander et al., 2007).

Finally, there is a clear release of water mostly at low temperature (Fig. 15c) recorded simultaneously at
masses 18 and 17 (OH). Both peaks are broad with long tails suggesting that water had condensed in the pipes
between the extraction furnace and QMS. We, however, believe that the low temperature release pattern of
water is basically not far from its true release in spite of water condensation on cold parts of the vacuum system.
This conclusion is based on the result of analyses of sodium bicarbonate which we used to evaluate the water
content in the meteorite samples. With the QMS sensitivity factor obtained for water (see section 3.3.4) we
calculated the total water content in the Allende standard using mass 17 to be 0.11 wt. %, which is in the range
obtained for this meteorite earlier, 0.11-0.16 wt. % (Robert and Merlivat, 1977) and 0.24 wt. % (Eiler and
Kitchen, 2004).

5.2. Murchison

2.02 mg of the Murchison sample was also analysed by QEGA. The pressure variations show basically a
single broad peak with a spike at 690 °C (Fig.16a). The release of most of major gases follow generally the same
pattern. The signal at masses 44 and 28 are mostly overlapping, though in detail, considering signals at masses
12 and 16, one can conclude that CO$_2$ is dominating in the temperature range 200-500 °C, while CO in the range
500-1000 °C (Fig. 16b). For both gases there is a spike at 690 °C. In a sense this is similar to what was observed
for CO$_2$ and CO releases from Allende, though without such an extensive overlap. It is considered likely that
release of these gases occurs due to chemical reactions between carbon and oxygen containing phases. The spike is obviously an indication of changing in the rate of the reactions A small signal at mass 16 at very high (>1200 °C) temperature not supported either by a signal at mass 28 or at mass 44, is probably due to methane.

Release of SO$_2$ is bimodal (Fig. 16d) and observed in the similar manner to that for Allende temperature range, indicating the presence of a similar sulphur containing mineral(s) in both meteorites. A peak of pure oxygen is also observed at very high temperature similar to that in case of Allende and has the same nature associated with SiO$_2$ vapours from the quartz extraction tube. Water is released mostly at relatively low temperature (Fig. 16c), but at higher concentration than for Allende. In general, the volatiles content in Murchison is significantly higher than in Allende, which can be seen in the signal intensities as well as in the total pressure recorded, especially considering that the sample size of the latter was larger by a factor of 1.5 compared to the former. This difference seems to be in line with the metamorphic grade of the meteorites (CM2 and CV3), consistent with the loss of volatiles during parent body metamorphism.

Figure 16. Release patterns of different gas species (b-d) and pressure variations (a) during EGA of the Murchison meteorite standard with heating rate 12 °C/min. Numbers next to curves indicate m/z.

Calculation of C concentration in the sample using signal at mass 16 as the measure of CO$_2$ amount and at mass 12 for CO amount gave the total amount of C higher than expected: 5.4% vs. ~2% (Mortimer et al., 2017). Similar discrepancy is obtained for water content: 20% vs. ~8% (Robert and Epstein, 1982; Jarosewich, 1971). The reason for such differences is currently not fully understood. This may be because mass 12
represents not only CO but has some contribution from CO₂. This could also be due to a contribution of other species such as methane on mass 16. The other explanations could be that during analysis of the sample the pressure in the QMS was quite high and therefore the overall conditions (in particular element fractionation in the QMS) were different from those that have been during calibration. The difference in the pressure conditions can also affect condensation of water and, therefore, it was different from that for the reference sample. All these possibilities will be investigated in our further development of the method. For hydrogen, which, in contrast to Allende, is released together with other major gases, we obtained a reasonable concentration, 0.06 wt. %, which is close to the range for this meteorite: ~0.1 (Alexander et al., 2010) and 0.074 wt. % (Kerridge, 1985). Close to the expected concentration we also obtained for nitrogen using signal at mass 14: 0.07 % vs. 0.08% (Mortimer et al., 2017).

6. Concluding remarks

We consider this study as a first step towards quantitative EGA of extra-terrestrial samples. A method of QMS calibration with reference gases (pure or gas mixture) with known flow rate has been developed along with flow rate calibration procedures. Testing the method with chemical compounds that can be thermally decomposed into gaseous components with well-known yields demonstrated accuracy though not particularly precise results. Future work will focus on improving the precision. For example, for major masses such as 2, 18, 28, and 44 could be measured using Faraday cups, while the minor masses could be registered using electron multipliers. In such cases, the multiplier saturation effect can be avoided and the signal to noise ratio for minor masses can be increased using a higher multiplier voltage. Along with the calibration we have developed an approach for more reliable identification of gas species in the multicomponent mixtures based on the analysis of mass spectra of the first and second order signals of certain gases. The application of the developed EGA to the meteorite standard samples of Allende and Murchison in most cases yielded reasonable results. However, the method requires further development and improvement, in particular for water measurements. These would benefit from a vacuum system that can be fully heated to ~120 °C to reduce condensation of water on internal surfaces and thus increase the efficiency of transfer to the QMS. A similar system has already been built in our laboratories for different purposes and provision for such heating has been made in the ProSPA instrument which will attempt QEGA in situ on the Moon within the Luna-27 mission.

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References:


The paper describes a quantitative evolve gas analysis with application to two meteorite samples. The method is based on calibration of the quadrupole mass spectrometer sensitivity with respect to different gases using flows of pure gases and gas mixtures as references which flow rates were determined by an independent method. The method was verified by analyses of pure chemical compounds decomposing into simple gases upon heating.
AUTHOR DECLARATION

We wish to draw the attention of the Editor to the following facts which may be considered as potential conflicts of interest:

Drs Sheridan and Morgan are employees of The Open University and are founders/directors of Applied Science & Technology Solutions Ltd that has a Manufacturing License Agreement with The Open University to commercialise the patented PZT valve. They are both named inventors on the OU patent. The valves used in this study were manufactured at The Open University.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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