Development of a low-cost tool for the compositional measurement of gases derived from mineral water wells from the Eastern Carpathians

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Abstract. The Eastern Carpathians host CO₂-rich, low temperature, dry gas vents, bubbling pools and wells/drillings, which were established for the extraction of mineral water and CO₂ for the bottling industry. These wells can provide important information on the structure of the geological deposits, the depths, and the source of the gases, because they are often located at important geologic/tectonic sites. Our aim was to test the applicability of a hand-made and low-cost tool in preselected wells/drillings, in order to measure the concentration of different gas species. This was challenging due to the high water and gas discharge of the wells, and their intermittent behavior. The method made possible the separation of gas and water phase, the extraction of gas, and the measurement combined with a Multi-GAS portable device. The hand-made barrel technique, and the closed cell for gas and water phase separation, proved to be a suitable and cheap tool to gain information about the CO₂, CH₄, and H₂S concentration of the gases derived from the wells/drillings.

Keywords: multi-GAS, CO₂, CH₄, H₂S, wells, low-cost tool

INTRODUCTION

Gas-vents, according to their origin are usually categorized by temperature and specific chemical composition. These can be fumaroles, solfataras, which are high temperature CO₂, H₂S, and SO₂ rich emitters; mofettes are cold CO₂ rich emitters, while mud volcanoes are mostly characterized by CH₄. These gas emissions are strongly influenced by the geological and tectonic setting of the specific area (Chiodini et al., 2004; Bräuer et al., 2008, 2016, 2018; Oppenheimer et al., 2014; Lee et al., 2016; Tamburello et al., 2018).

In Romania, the Neogene-Quaternary volcanic chain of the Eastern Carpathians and its neighboring geological units are characterized by CO₂-rich, cold gas emissions, that occur in the form of dry gases, namely mofettes, bubbling pools and wells (Airinei and Pricăjan, 1970; Althaus et al., 2000, Vaselli et al., 2002, Jánosi et al., 2011; Kis et al., 2017, 2019, 2022). Recent surveys demonstrated that at the proximity of the Ciomadul volcano, the youngest volcano of the Eastern Carpathians, the annual CO₂ output is 8700 t/y, which is comparable to other volcanic systems of similar age (Kis et al., 2017).

Our research area is characterized by extensive mineral water exploitations. Our research sites are situated in vicinity of several major exploitation plants that hold nearly 60% of the Romanian bottled, sparkling mineral water market. (e.g., Perla Harghitei, Tușnad, Borsec etc.). Most of the exploitation wells were established in the middle of the 20th century as exploratory boreholes to study the main hydrogeological features of the area and for prospecting mineral water and free CO₂ for the bottling industry (Fig. 1; Feru, 2012).

The mineral waters represent the drinking water supply of the local population, who consume them on a daily basis (Jánosi et al., 2011; Feru, 2012). Wells are situated in important locations like bottling factories (Feru, 2012). In addition to the mineral water potential of the area, another important factor is the therapeutic value of the gases and mineral waters, which are used in physical, balneological and cardiological treatments at several locations e.g., Băile Tușnad, Covasna (Incze et al., 2017). The primary motivation of our work was to test the applicability of a tool, designed and built by us to gather real time and in-situ information on the chemical composition of the gases derived from open wells/drillings present in the study area. We coupled our home-made tool to an instrument which is capable for the in-situ compositional measurement of the low-temperature gases, the Multi-GAS (Kis et al., 2022).

The development of the Multi-component Gas Analyzer System (Multi-GAS) began in the early 2000’s with the purpose to create an instrument that provides real-time data on the compositional changes of the fluids released from different types of manifestations. The application of the Multi-GAS systems are numerous, especially in active volcanic areas (Aiuppa et al., 2005). The instrument can be used either as a portable meter or as a permanent station (Aiuppa et al., 2005; Shinohara et al., 2015). Portable instruments are used for field surveys, temporal/spatial compositional mapping of the gas emissions (Aiuppa et al., 2005; Allard et al., 2014). Multi-GAS instruments as permanent stations are also used for short- or long-term monitoring (Aiuppa et al., 2005, 2007, 2014, 2015; Shinohara et al., 2015; Moussallam et al., 2017).
At dormant volcanic areas, investigations are involving studies on the gas dynamics (Norris Geyser basin, Yellowstone, Lewicki et al., 2017), monitoring and evaluating of the effect of environmental factors like wind speed, groundwater level changes and barometric pressure on the gas levels, compositions, and debit. These investigations are important because the dormant volcanic systems sometimes are densely populated locations, where people are directly exposed to the gas emissions (Allard et al., 2014; Viverios et al., 2016).

Measurements with Multi-GAS may offer fast and accurate data collection and it is widely used at active volcanic areas (Aiuppa et al., 2005, 2007, 2014, 2015; Shinohara et al., 2015). While natural dry and bubbling gas emissions are relatively easy to measure with the Multi-GAS (Kis et al., 2022), wells often represent a challenge due to their high water and gas discharge, intermittent nature or due to their structure often difficult to reach (Fig. 2). Despite these difficulties, wells represent important sites in our study area, because they are situated at important locations from a geological point of view, such as tectonic lineaments and degassing sites with high flux. These tectonic features facilitated the upwelling of CO$_2$-rich deep groundwater suitable for the bottling industry (Feru, 2012).

**GEOLOGICAL BACKGROUND**

The main study area is in the youngest volcanic chain of the Eastern Carpathians (Călimani-Gurghiu-Harghita), and its neighboring geological units, such as the sedimentary units of Transylvanian Basin, the intra-Carpathian Ciuc and Gheorgheni basins, the Cretaceous to Paleogene Flysch and the Precambrian and Cambrian metamorphic units (Fig. 1).

The metamorphic units are of Precambrian and Cambrian age, represented by medium and high-grade metamorphic rocks that are mostly affected by hydrothermal alternations and in some cases thermal metasomatism (Mosonyi, 1998; Ureche, 1999).

**Fig. 1.** The geological map of the researched area and the locations of the measurements, marked as following: 1: Bálványos sósmező Drilling, 2: Remetea, 3: Covasna-Central Spring, 4: Slănic Moldova Spring, 5: Vlahița Drilling, 6: Cetățuia Spring, 7: Antalkáék Bath, 8 - Tușnad-Bagoly Spring, 9 - Sâncrăieni-Drilling. Geological base map reproduced after Alexandrescu et al., 1968; Joja et al., 1968; Patrulius et al., 1968; Vasilescu et al., 1968; Dumitrescu et al., 1970a, b; Săndulescu et al., 1971, 1973; Popescu et al., 1975; Peltz et al., 1984).

The Cretaceous and Paleogene Flysch cover almost the 75-80% of the Romanian segment of Eastern Carpathians and can be grouped into two main units: an Inner Flysch (Ceahlău and Teleanjen nappes) and an Outer Flysch belt (Audia, Târcau and Vrancea nappes). The sediments are dominated by alternation of calcareous sandstones, marls, limestones, clays, and sandstones (Mațenco and Bertotti, 2000; Mutihac et al., 2004; Mațenco et al., 2007).

The volcanic activity of the youngest volcanic chain of the Carpathian Mountains took place between 11.3 and 0.03 million years ago (Pécskay et al., 2006; Molnár et al., 2018). The development of the Călimani-Gurghiu-Harghita Neogene and Quaternary volcanic area is related to the most recent post-collisional stages of the Carpathian-Pannonian region and the inner Carpathian volcanic belt (Seghedi et al., 1995; Pécskay et al., 2006).

The Călimani-Gurghiu-Harghita is the longest continuous volcanic chain of the Carpathians, its length is reaching approximately 160 km, oriented to North-South, also the chronology of activity evolved in this direction. Composition of the volcanic structures of the above-mentioned area is dominated by andesites, dacites and in rare cases shoshonitic rocks (Seghedi et al., 2004, 2011).
The formation of the intra-Carpathian basins can be related to the Neogene and Quaternary volcanic activity of the area. They sunk and were filled with volcanic debris, epi- and pyroclastites due to the geodynamic activity of the area (Csontos et al., 1992; Mațenco and Bertotti, 2000; Mațenco et al., 2007). The base of the above-mentioned basins was created by sandstone- and marl-dominated sediments which were connected to the neighboring Cretaceous flysch sedimentary units (Mureșan and Szakács, 1998; Mutihac et al., 2004).

**METHODOLOGY**

In our investigation we used a specially designed portable Multi-GAS for low-temperature, CO₂-rich gas emissions, described in detail in Kis et al. (2022). The instrument was equipped with two specific Gascard II IR spectrometers for determining CO₂ (0-100% range) and CH₄ (0-5% range) and one electrochemical sensor for H₂S (0-200 ppm range) analysis. The gas was collected and pumped simultaneously and constantly through the detectors. The measurement took several minutes, depending on the flux of the different emissions. The final concentration results of the measurements made with the Multi-GAS device were calculated in Microsoft Excel (MS Office) by averaging the stable plateau.

In the case of wells, where the free CO₂ rich gases often come to surface together with the water, in order to gather appropriate data, we used a specially designed hand-made tool, a very simple barrel, that was attached to the well output. The construction of this method was simple, the prototype used was developed primarily based on field experiences and ideas. The barrel was tested during several field surveys between October of 2019 and September 2021 across the Eastern Carpathians. The main goal was to be able to separate the free gas and water phases that are leaving the wells together, the water is oversaturated and it cannot dissolve more gas phases, so the gas leaves freely the wells in the form of bubbles. The principle was that the CO₂-rich gases are much denser than the air, so they accumulate in the lower segment of the space. The construction of the barrel provided space for this. Water and free gas released from the well came through a single tube, in the barrel the separation of the two phases occurred, and two separate outputs ensured the removal of the water and the separated gas-phase. In the barrel the separation of the gas phase from the water took place and the gas output was connected to the instrument (Fig. 3).

![Fig. 2. Images of selected sites listed in Table 1 with the following codes: a = 1, b = 2, c = 5, d = 7, e = 8, f = 9.](image1)

![Fig. 3. The structure and the field application of the barrel separation cell at the Site #2 (see Table 1).](image2)
The water output was at the bottom of the barrel, where we were able to create and control a constant water level in the structure, which was important to avoid air contamination. The gas outlet was placed at the top of the barrel, to which we could directly attach the input unit of the Multi-GAS. Measurements could be controlled in the field, and final concentration values were calculated from the average of the stabilized values (Fig. 4).

![Fig. 4. The in-situ measurement curves of the CO\textsubscript{2}, CH\textsubscript{4}, and H\textsubscript{2}S concentrations of the free gases from well with ID #5 cell at the site #2 (see Table 1).](image)

RESULTS AND DISCUSSION

We investigated 9 mineral water wells, with the help of the combined Multi-GAS and hand-made barrel methodology. The IDs, site names, locations, measurement quality, geographical coordinates, and the concentrations of CO\textsubscript{2}, CH\textsubscript{4}, and H\textsubscript{2}S are listed in Table 1.

In five times from the nine listed measurements, we received stable results without air contamination. These measurements could not have been performed without the presence of this hand-made tool.

In several cases, the drillings were situated at a relevant geographical location that can assist to investigate the relationship between gas vents and tectonic elements of the area, e.g., site ID #3 is located along the extensional fault line that appears in the center of city Covasna (Dumitrescu et al., 1970b). In the case of the wells studied in the vicinity of Ciomadul the youngest volcano in the Eastern Carpathians, a thermal anomaly is observed. The temperature of the water from wells were higher compared to the other sites: at the site ID #1, 15°C and at site ID #7, 26°C water temperature was measured (Demetrescu and Andreescu, 1994).

Measurements were primarily influenced by the water and gas discharge from the wells and their continuous or periodic behavior. In the case of site ID #1 and ID #2 the water discharge stopped for more than 10 minutes, but the quiet period had no effect on free gas, that was persistent. We managed to solve the problem of different water yield by changing the diameter of the water output, that needed to be adapted to each location.

Comparing the concentrations of different gas species gained with the barrel technique, with compositional information of the natural gas emissions located close to these wells (Vaselli et al., 2002; Kis et al., 2019), the data show similarities e.g., close location with ID #1, Kis et al. (2019) measuring 95.24% as CO\textsubscript{2} concentration and Vaselli et al. (2002) 95.63%, which not only increases the validity of the technique, but also proves to be a useful tool for quantifying new information. The results obtained are consistent with other techniques and manifestation types of gas vents in the study area and the concentrations can be grouped according to the geological context. Based on the results, the CO\textsubscript{2} is the dominant component (exception is represented by ID #4, that is located at Slănic Moldova, close to hydrocarbon reservoirs) in the measured gases. The concentration values of CO\textsubscript{2} vary between 0.43-100%, the lowest value was measured in ID #4, and the highest concentrations in ID #2 and #3. High values (>90%) were measured at the volcanic units (Harghita Mts.) and the intra-Carpathian basins (site ID #1, 2, 5, 6, 7, 8, and 9), but also in the sedimentary structures of the Paleogene Flysh (site ID #3), which suggests a possible tectonic control on the gas emissions (Kis et al., 2017). The lowest value was measured in the hydrocarbon-hosted area of the Paleogene Flysh, at Slănic Moldova (ID 4), where the CH\textsubscript{4} was the main component. According to literature, the origin of CO\textsubscript{2} is mainly (~60%) related to mantle derived fluids (Althaus et al., 2000; Vaselli et al., 2002; Kis et al., 2019). In the case of the CO\textsubscript{2} concentration of well with ID 1, our results were confirmed by previous measurements with gas-chromatography (79.78 and 80.62%; Kis et al., 2019). The most studied dry gas vent of the area is the Torjai Stinky Cave, which is in the vicinity of the drilling (ID 1), which also serves as a reference point for the performed measurement, concentration data reported a similar CO\textsubscript{2} composition 98.3% (Vaselli et al., 2002). In the case of well ID #3, the CO\textsubscript{2} concentration reached a value close to 100%. In the proximity of this well, located at Covasna, several Health Care Centres were established with other wells and artificial mofettes. Wells with ID #6,7, 8, and 9 appear on the tectonic lineament of the Olt River, close to several important mineral springs and gas emissions e.g., sites ID #8 and #9 are located near two large bottling plants (Tușnad and Perla Harghitei) in Romania (Feru, 2012).
The CH₄ concentrations ranged between 0.21 and 7% and were higher next to the hydrocarbon-prone areas, such as the previously mentioned sedimentary deposits of the Cretaceous and Paleogene Flysch reaching values above the detection limit of our detector (7%) (e.g., Site ID #4). The origin of CH₄ in the research area is described as thermogenic (Ionescu et al., 2017; Baciu et al., 2018).

Table 1. The CO₂, CH₄, and H₂S concentrations and the water temperature of the analyzed wells with barrel technique (Data from Kis et al. 2020).

<table>
<thead>
<tr>
<th>ID</th>
<th>Site name</th>
<th>Location</th>
<th>Measurement quality</th>
<th>Longitude</th>
<th>Latitude</th>
<th>H₂S (ppm)</th>
<th>CH₄ (%) ± 2</th>
<th>CO₂ (%) ± 2</th>
<th>Water temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bálványos sósmező</td>
<td>Băile Balvanyos</td>
<td>No air contamination</td>
<td>25.94238</td>
<td>46.11598</td>
<td>26.6</td>
<td>0.4</td>
<td>95.4</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>Remetea</td>
<td>Remetea</td>
<td>No air contamination</td>
<td>25.44949</td>
<td>46.779974</td>
<td>0</td>
<td>0.7</td>
<td>100</td>
<td>12.6</td>
</tr>
<tr>
<td>3</td>
<td>Covasna- Central Spring</td>
<td>Covasna</td>
<td>No air contamination</td>
<td>26.170368</td>
<td>46.170368</td>
<td>16.8</td>
<td>0.5</td>
<td>100</td>
<td>11.7</td>
</tr>
<tr>
<td>4</td>
<td>Slănic Moldova Spring</td>
<td>Slănic Moldova</td>
<td>No air contamination</td>
<td>26.427974</td>
<td>46.202235</td>
<td>0</td>
<td>7</td>
<td>0.4</td>
<td>11.2</td>
</tr>
<tr>
<td>5</td>
<td>Vlăhița- Drilling</td>
<td>Vlăhița</td>
<td>No air contamination</td>
<td>25.50298</td>
<td>46.32707</td>
<td>12.2</td>
<td>0.9</td>
<td>99.5</td>
<td>13.2</td>
</tr>
<tr>
<td>6</td>
<td>Cetățuia- Spring</td>
<td>Cetățuia</td>
<td>Air contaminated</td>
<td>25.89774</td>
<td>46.240476</td>
<td>4.08</td>
<td>0.2</td>
<td>83.1</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>Antalkák Bath</td>
<td>Bixad</td>
<td>Air contaminated</td>
<td>25.85283</td>
<td>46.1415</td>
<td>0.03</td>
<td>0.8</td>
<td>79</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>Tușnad- Bagoly Spring</td>
<td>Tușnad</td>
<td>Air contaminated</td>
<td>25.916042</td>
<td>46.204471</td>
<td>1.8</td>
<td>1.5</td>
<td>31.2</td>
<td>11.6</td>
</tr>
<tr>
<td>9</td>
<td>Sâncraieni- Drilling</td>
<td>Sâncraieni</td>
<td>Air contaminated</td>
<td>25.847336</td>
<td>46.303585</td>
<td>3.01</td>
<td>0.4</td>
<td>49.5</td>
<td>13.1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

With help of the hand-made barrel technique, we were able to create a methodology for the in-situ gas-compositional measurement of gas bearing mineral water wells. In the barrel, the separation of the gas and water phase took place and provided the safe measurement of the concentrations of CO₂, CH₄, and H₂S of the gas emissions with the use of the Multi-GAS instrument. We were able to test the method at nine wells of different types and different geological units within the Eastern Carpathians. The obtained measurements were in good agreement with previous investigations performed on natural gas emissions, such as dry gases-mofettes and bubbling pools. The barrel method provides an opportunity to investigate these mineral water wells, which were established at important geological sites, e.g., at tectonic lineaments.

Compositional studies can provide a detailed overview on the gas-geochemical context of the area and help to interpret the relationship between gas flows and tectonic units. The Multi-GAS instrument proved to be a useful tool not only at active volcanic areas but also in the study of the gas emissions of the Eastern Carpathians.

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REFERENCES


