

EUROVOLC

European Network of Observatories and Research Infrastructure for Volcanology

Deliverable Report

D5.1: Best practices – fumarolic gases

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Summary

This report summarizes the activities developed in the framework of Task 5.1 (WP5) with the aim to contribute to the definition of best practices in direct sampling of fumarolic gases. Several direct sampling techniques have been applied in the study of volcanic gases. However, the so-called Giggenbach methodology has been widely used as a preferential method to obtain complete gas analyses of the gases released in fumaroles, independently of the outlet temperatures.

Considering that variability of the results may be explained by several factors, related not only to the sampling, but also to the analytical procedures or even to the data treatment, recommendations of best practices associated with this direct sampling methodology are challenging, as they should account for a significant variety of possibilities.

Several activities were carried out under the umbrella of the EUROVOLC project to characterize the consortium facilities, as well as, to perform intra and inter-laboratorial comparisons. The main activities are synthesized below:

1. Two queries shared between partners to evaluate differences/similarities related to the sampling and analytical methodologies
2. A joint survey was carried out at the hydrothermal fumarolic field of Furnas Volcano (Azores archipelago) in February 2019. Gases were collected in a low temperature fumarole following the Giggenbach methodology. Seven entities were involved (CIVISA, IGN-CSIC, IMO, INGV, IPGP, OPGC, UNIVLEEDS) and resulted in 20 gas collections and analyses from the same site.
3. Web meetings to discuss the data obtained and define strategies to face the difficulties due to the pandemic scenario (May and June 2020; March 2021).
4. Intra-laboratorial surveys performed during 2020 by CIVISA and IPGP-OVSG to discriminate differences associated with the pre-sampling (preparation of the gas bottles) and analytical strategies. The surveys were done on Furnas Volcano (Azores archipelago) and La Soufrière Volcano (Guadeloupe), resulting in 24 additional gas analyses from low temperature fumaroles.
5. Preparation of reports that contributed to the data evaluation and definition of possibilities for the data treatment.

1) Introduction

Several field surveys based on the so-called Giggenbach methodology have been done in the last thirty years to contribute to establishing comparable measurements between different research teams. The Commission on the Chemistry of Volcanic Gases (CCVG) team from the International Association of Volcanology and Chemistry of the Earth's Interior (IAVCEI) has widely contributed to these joint fieldworks, which were carried out in several volcanic areas, by international teams, for a total of 13 workshops until 2021. Data obtained in the first five workshops and in the 12th workshop were published and discussed (Corazza, 1986; Mazor *et al.* 1988; Giggenbach and Matsuo, 1991; Giggenbach *et al.*, 2001; Lopez *et al.*, 2018). For most of the recent workshops, the integration of the results obtained with the above-mentioned technique is missing in the literature. Despite all the technical improvements, including the facilities associated with remote sensing, it is widely accepted by the volcanological community that direct sampling using the Giggenbach methodology appears to be the best way to provide a complete chemical analysis of fumarolic gases. In fact, results obtained from direct sampling in fumaroles are applied in volcanic monitoring by volcano observatories worldwide, including modelling of the thermodynamic conditions of geothermal reservoirs.

Despite several efforts made in the past to compare data obtained through the above-mentioned technique, challenges persist as several variables may interfere with the results. Consortium partners agree that the introduction of variability in the results may be associated with several factors, such as (1) the sampling preparation, (2) the sampling itself (which can be affected not only by operator aspects but also by changes of fumarole fluxes and potentially by different configurations of the sampling pipeline), (3) the modality and the timing of preservation/storage of the sample, (4) the analytical procedures or even (5) the data evaluation. The complexity of the involved variables recalls the need for a very careful evaluation of the data and an unpretentious list of recommendations that can eventually contribute to improving some of the procedures.

Our consortium is aware of the limitations of these recommendations and the fact that our suggestions particularly apply to hydrothermal fumaroles, with similar characteristics (*e.g.*, temperature, composition fluxes, etc.) as the ones sampled during the survey at Furnas Volcano. Still, we hope that the recommendations that we give, based on some lessons we learned, may be useful for researchers not only from the consortium but also in the wider volcanological community.

2) Activities carried out under the EUROVOLC project

2.1) State of the art of the EUROVOLC partners

2.1.1) Characterization of the consortium facilities for direct sampling in fumaroles

A first query shared between all partners aimed at identifying which observatories-research teams would be involved in the direct sampling using the so-called Giggenbach methodology. This query was also used to prepare the fieldwork carried out at Furnas Volcano (São Miguel Island) in February 2019. Ten teams participated in the survey and eight of them confirmed that they commonly perform direct sampling measurements in fumaroles (Table 1). However, only six teams (CIVISA, IMO, IGN – CSIC, INGV-Pa, INGV-OV and IPGP-OVSG) carry out measurements using the so-called Giggenbach methodology (Giggenbach, 1975), namely using evacuated flasks with a soda solution (in this case, all the teams use NaOH 4M). None of the teams are currently using KOH as the basic solution.

Table 1. Query shared between the partners to characterize the consortium capacities in terms of direct sampling.

1. Please identify your research team (Institute, Country)	CIVISA	IMO	IGN - CSIC	INGV-Pa	INGV - OV	IPGP - OVPF	IPGP - OVSG	UCA-OPGC	University of Leeds	University of Manchester
2. Does your research team perform direct sampling in the fumaroles?	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	No	Yes
3. Does your research team has laboratorial facilities to perform analyses of the gases collected in the fumaroles?	Yes	No	No	Yes	Yes	No	Yes	Yes	No	No
SAMPLING PHASE										
<i>Please answer the following questions if you answered YES on question 2.</i>										
4.1. If you answered others to question 4., please specify?										
4. Which methodology your team uses to sample the fumaroles?	Giggenbach method + Multigas	Giggenbach method + Multigas	Giggenbach method	Giggenbach method + Multigas	Giggenbach method	MultiGas + FilterPack + bag sampling	Giggenbach method + Multigas	Multigas		<i>in-situ</i> TDLS
5. If you use Giggenbach bottles to sample, do you collect...?	both soda and dry samples	both soda and dry samples	both soda and dry samples	both soda and dry samples	both soda and dry samples	n.a.	both soda and dry samples	MultiGas + impregnated filters + raw		n.a.
6. How do you collect the gas? With funnel or tube inserted in the vent?	Funnel	Both Funnel and Probe	Probe	Probe	Both Funnel and Probe	n.a.	Probe	No		Open-path <i>in-situ</i>
7. Do you use any condenser to trap the water vapour in the dry sampling surveys?	Yes	No	Yes	Yes	Yes	n.a.	Yes	No		no

From the above-mentioned teams, only four (CIVISA, INGV-Pa, INGV-OV and IPGP-OVSG) have laboratory facilities to analyse the gases collected with the Giggenbach method. Sampling apparatus may also be diverse between teams, with differences, for instance, related to the use of funnel or probe to sample the gas. These differences are essentially site-dependent and are related to the type of gas emissions. Most of the teams informed they used a condenser to trap the water for the dry samples.

After the joint survey in February 2019, a new query was shared between the four teams that have laboratory facilities to analyse the gas collected. The questions were mainly related to the analytical procedures used for each of the analysed species, the instrument brands and models used, the accuracy and limits of detection/quantification (when available), the standards used and whether previous inter-laboratory comparisons were done (Table 2).

Table 2. Query shared between the partners that have laboratory facilities (CIVISA, INGV-Pa, INGV-OV, IPGP-OVSG) to analyse the gases collected in fumaroles.

Questions - TASK 5.1 WPS																
1. Please identify your laboratory																
1.1. Name of the responsible for the analytical procedures																
1.2. Name of the responsible of the laboratory (and that confirms the analyses)																
ANALYTICAL PHASE																
	H ₂ O	CO ₂	H ₂ S	⁴⁰ Ar	O ₂	N ₂	CH ₄	H ₂	He	CO	⁴⁰ Ar/ ³⁶ Ar	δ ¹⁵ N	δ ¹³ C _{CO2}	δ ¹⁸ O _{CO2}	δ ¹⁸ O _{H2O}	δ ² H _{2O}
2. Based on the above gas species, which method (Chromatography, titration...) you use to analyse each of the gas species?																
3. Name the instrument used to analyse each gas specie																
3.1. Refer the brand of the instrument referred on point 3.																
3.2. Refer the model of the instrument																
3.3. Refer the accuracy of the measurement (for each specie), if known																
3.4. Refer the limit of detection/quantification of the measurement (for each specie), if known																
4. Which standard you use for each of the gas specie (for instance, gas bottles with a specific mixture of gases that should be mentioned; known concentration of gas in a solution...)																
5. Is this the first time you perform inter-laboratorial comparison of analyses?																
6. Please share bibliographic references where the methodology used in your laboratory is described.																

All four laboratories analyse the main gas species (H₂O, CO₂, H₂S, Ar, O₂, N₂, He, CO and CH₄), excluding CIVISA which does not have facilities to detect CO. INGV-Pa does not determine Ar. Only INGV partners were able to analyse dry gases and to carry out isotopic measurements.

Table 3 shows the methods used to analyse the different gas species by each laboratory. Only CIVISA uses a distinct method to analyse H₂S (titration with mercury acetate). All the other laboratories use ion chromatography. None of the teams use Cd methodology (Montegrossi *et al.*, 2001) to favour precipitation of H₂S and quantify the different sulphur species. For the specific case of the Furnas hydrothermal fumaroles, this aspect is not relevant as the sulphur compounds correspond to the H₂S.

Table 3. Analytical methods used by the different teams to analyse each of the gas components (*n.d.* – not detected).

Gas species	CIVISA	INGV-Pa	INGV-OV	IPGP-OVSG
H ₂ O	Weight	Weight	Weight	Weight
CO ₂	Potentiometric Titration	Potentiometric Titration	Potentiometric Titration	Potentiometric Titration
H ₂ S	Colorimetric Titration	Ion Chromatography	Ion Chromatography	Ion Chromatography
⁴⁰ Ar	Gas Chromatography	Gas Chromatography	Gas Chromatography	Mass Spectrometry
O ₂	Gas Chromatography	Gas Chromatography	Gas Chromatography	Mass Spectrometry
N ₂	Gas Chromatography	Gas Chromatography	Gas Chromatography	Mass Spectrometry
CH ₄	Gas Chromatography	Gas Chromatography	Gas Chromatography	Mass Spectrometry
H ₂	Gas Chromatography	Gas Chromatography	Gas Chromatography	Mass Spectrometry
He	Gas Chromatography	Gas Chromatography	Gas Chromatography	Mass Spectrometry
CO	<i>n.d.</i>	Gas Chromatography	Gas Chromatography	Mass Spectrometry
⁴⁰ Ar/ ³⁶ Ar	<i>n.d.</i>	<i>n.d.</i>	GC-IRMS	<i>n.d.</i>
δ ¹⁵ N	<i>n.d.</i>	<i>n.d.</i>	GC-IRMS	<i>n.d.</i>
δ ¹³ C _{CO2}	<i>n.d.</i>	IRMS	IRMS	<i>n.d.</i>
δ ¹⁸ O _{CO2}	<i>n.d.</i>	<i>n.d.</i>	IRMS	<i>n.d.</i>
δ ¹⁸ O _{H2O}	<i>n.d.</i>	Laser Spectroscopy	IRIS WS-CRDS	<i>n.d.</i>
δ ² H _{H2O}	<i>n.d.</i>	Laser Spectroscopy	IRIS WS-CRDS	<i>n.d.</i>

Table 4. Standard procedures used by the different teams (n.d. – not detected).

Gas species	CIVISA	INGV-Pa	INGV-OV	IPGP-OVSG
H ₂ O	-	-	Internal calibration	-
CO ₂	pH standards solutions: 7.000 ± 0.010 Buffer Radiometer analytical; 4.005 ± 0.010 Buffer Radiometer analytical. Concentration of the acid: 0.1 N HCl	pH standards solutions: 7.000 ± 0.010 Buffer Merck analytical; 4.005 ± 0.010 Buffer Merck analytical. Concentration of the acid: 0.1 N HCl	Normalized solution	-
H ₂ S	-	6-point calibration: #1=1.91ppm; #2=3.82ppm; #3=7.48ppm; #4=18.20ppm; #5=34.50 ppm; #6=62.90 ppm.	Dionex® standards	Sulfate standard solution 1000ppm
⁴⁰ Ar	Gas bottle with a specific mixture of gases: 3.00% Ar, 2% O ₂ , 5.00% CH ₄ , 4.03%He, 35.99% H ₂ , rest N ₂	-	Pure gas, gas mixture	SO ₂ 1.011 %, rest Ar (Praxair); H ₂ S 1.01 %, rest Ar (Praxair); CO 1.8 %, rest Ar (Messer)
O ₂		3 Gas bottles with a specific mixture of gases: Bottle #1: O ₂ :0.38%; N ₂ :1.62%; CH ₄ :0.00051%; He:0.00103%; H ₂ :0.00103; CO:0.00051% Bottle #2: O ₂ :5.99%; N ₂ :35.01%; CH ₄ :0.01%; He:0.0101%; H ₂ :0.0101; CO:0.01%. Bottle #3: O ₂ :10.08%; N ₂ :88.92%; CH ₄ :0.101%; He:0.0424%; H ₂ :0.0890; CO:0.0998%		CH ₄ 1.011 %, rest Ar (Messer)
N ₂				He 0.5002 %, rest N ₂ (Messer)
CH ₄				CO ₂ 10 %, H ₂ 10.01 %, rest N ₂ (Messer)
H ₂				He 0.5002 %, rest N ₂ (Messer)
He				CO 1.8 %, rest Ar (Messer)
CO	n.d.			
⁴⁰ Ar/ ³⁶ Ar	n.d.	n.d.	Air, pure gas	n.d.
¹⁵ N	n.d.	n.d.	Air, pure gas	n.d.
¹³ C _{CO2}	n.d.	2 reference gas bottles. Ref#1: ¹³ C=0.63‰; Ref#2: d13C=6.67‰; vs. PDB	Working standards vs. V-PDB	n.d.
¹⁸ O _{CO2}	n.d.		Working standards vs. V-PDB	n.d.
¹⁸ O _{H2O}	n.d.	3 reference waters: Ref#1 ¹⁸ O= -11.38‰; Ref#2 ¹⁸ O= -8.61‰; Ref#3 ¹⁸ O= +4.16‰ vs. SMOW	Working standards vs. V-SMOV	n.d.
² H _{H2O}	n.d.	3 reference waters: Ref#1 ² H= -76.0‰; Ref#2 ² H= -49.9‰; Ref#3 ² H= +7.8‰ vs. SMOW	Working standard vs. V-SMOV	n.d.

For the gases detected on the headspace (Ar, O₂, N₂, H₂, He, CH₄), three laboratories use gas chromatography (GC), and IPGP-OVSG uses quadrupole mass spectrometry (QMS).

In what concerns the use of standards, the studied laboratories use different mixtures and calibration strategies (Table 4). The gas mixtures used for the calibration procedures for gas chromatography and mass spectrometry are different between the laboratories, not only due to the diverse instruments used, but also due to the characteristics of the gas samples usually analysed.

Aspects related to the accuracy and limit of detection/quantification of the different gas species were specified only by INGV-Pa. In what concerns previous inter-laboratory calibrations, only CIVISA and INGV-OV recognized that this type of approach was done previously.

All the additional information collected from query 2, which also comprises the brand and type of instruments used, as well as detailed information about the laboratory techniques, will support the metadata for the database elaborated in Task 5.3.

2.1.2) Furnas Volcano field survey: from sampling to the datasets

2.1.2.1 Sampling

Before selecting a volcanic area to perform a joint survey of direct fumarole sampling, a query sent to all the partners allowed the selection of São Miguel Island (Azores archipelago) as an adequate site to develop a common field survey for Task 5.1 activities. Furnas hydrothermal fumaroles (Furnas Volcano) were selected as they are already well characterized by the CIVISA team and are relatively easy to access and sample. In addition, the local partner was able to provide logistic support for the fieldwork organization, including permits for access to the Furnas Volcano fumarolic fields, transport in the field, and the use of laboratory facilities to prepare material and instruments. This activity was complementary to the first EUROVOLC Annual Meeting held in the Azores, which allowed participation by a greater number of individuals and saving of resources.

Nineteen researchers from seven institutions (CIVISA, CSIC, IMO, INGV, IPGP, UCA-OPGC, UNIVLEEDS) participated in the survey that was carried out at Furnas Volcano fumarolic fields. The direct sampling of the hydrothermal fumaroles was carried out at Caldeira Seca fumarole (Furnas village fumarolic ground) following the Giggenbach methodology. CIVISA laboratories were also used in the pre-sampling phase for the preparation of some of the Giggenbach bottles. During this survey, training of some of the participants was also possible, not only in the preparation of gas bottles, but also for the sampling.

The survey was carried out on the 21st and 22nd of February 2019 (Fig. 1). In what concerns direct sampling in the fumaroles, five teams (CIVISA, CSIC, IMO, INGV, IPGP) actively participated using the Giggenbach methodology. Each team sampled four gas soda samples and two dry samples, which were then sent to the geochemical laboratories that had facilities and had agreed to analyse the gas collected (i) in the soda samples (CIVISA, INGV-OV, INGV-Pa, IPGP-OVSG) and (ii) in the dry component (INGV-Pa, INGV-OV).



Figure 1. Collection of gases at Caldeira Seca fumarole during the EUROVOLC field activities carried out in the Azores archipelago in February 21st, 2019.

The sampling line was set up at the beginning of the survey and was the same for all the teams that collected soda samples on the 21st of February. At this site, since there is boiling water at shallow depth,

a funnel was placed in the fumarole and the gas directed to the Giggenbach bottle through silicon tubes. An individual from each team sampled the Caldeira Seca fumarole using the same gas line, but different sampling bottles with different volumes, forms and stopcocks were used. All teams used NaOH 4M as the soda solution, but the volume of soda solution was different in each bottle and prepared individually by each team. The time and duration of sampling are displayed in Table 5.

The dry gases were sampled on the 22nd of February at the same site where soda samples were collected. However, in this case, each team set up their own line for collecting the dry samples, in the same manner as they usually do.

We are aware that in addition to the natural variability of the fumarole during the Furnas survey several simultaneous non-controlled variables may have interfered with the results, namely diverse operators, distinct bottle types (format, dimension, and stopcocks), soda amount, time and duration of sampling, to give some of the examples. Nevertheless, the field survey provided an opportunity to identify together some of the variables that may contribute to the variability of the results.

2.1.2.2 Analytical procedures

Four laboratories analysed the results using not only different instruments (brands, models, precision), but also different techniques in some cases, as mentioned in the previous section. For instance, three laboratories carried out analyses on the gases present in the headspace by using gas chromatography, while one of the teams used mass spectrometry. CO is analysed in the soda sample by IPGP-OVSG and INGV-Pa, and in the dry bottle by INGV-OV. INGV-Pa also analysed CO in the dry bottles, however the gases analysed were below, or close to, the detection limit of the instrument. Specific techniques and methodologies used by the different partners are displayed in Table 3.

Table 5. Time and duration of sampling for the different teams.

Sampling Team	Ref.	Starting time	Finishing time	Sampling time
INGV-Pa	1	15:18	15:33	00:15
IGN-CSIC	2	14:11	14:29	00:18
IMO	3	15:50	16:08	00:18
CIVISA	4	16:10	16:28	00:18
IPGP - OVSG	5	12:47	12:58	00:11
INGV-Pa	6	13:38	13:50	00:12
IGN-CSIC	7	13:55	14:10	00:15
IMO	8	13:16	13:37	00:21
CIVISA	9	14:32	14:49	00:17
IPGP - OVSG	10	12:30	12:42	00:12
INGV-Pa	11	11:20	11:31	00:11
IGN-CSIC	12	12:12	12:22	00:10
IMO	13	11:44	12:09	00:25
CIVISA	14	11:34	11:41	00:07
IPGP - OVSG	15	11:07	11:17	00:10
INGV - Pa	16	15:34	15:47	00:13
IGN-CSIC	17	14:50	15:15	00:25
IMO	18	16:45	17:06	00:21
CIVISA	19	16:29	16:42	00:13
IPGP - OVSG	20	13:01	13:11	00:10

2.1.2.3 Results

Results shared during the EGU meeting in April 2019 by all the partners are displayed in Table 6. The table displays 20 complete chemical gas analyses for the gas compositions and a maximum of eight analyses resulting from the dry samples of Caldeira Seca fumarole (Furnas Volcano).

Table 6. Chemical analysis of the gases collected at Furnas Volcano fumarole, named Caldeira Seca, in February 2019. Reference numbers aim to facilitate the discussion in the current report (n.d. – not detected).

Laboratories	Sampling Team	Ref	H ₂ O (ppm)	CO ₂ (ppm)	H ₂ S (ppm)	Ar (ppm)	O ₂ (ppm)	Ar+O ₂ (ppm)	N ₂ (ppm)	CH ₄ (ppm)	H ₂ (ppm)	He (ppm)	CO (ppm)	⁴⁰ Ar/ ³⁶ Ar	δ ¹⁵ N	δ ² H _{H2O}	δ ¹⁸ O _{H2O}	δ ¹³ C _{CO2}	δ ¹⁸ O _{CO2}
CIVISA	INGV - Pa	1	955437	43931	447	1.17	3.09		67.7	1.99	109.7	1.13	n.d.						
	IGN - CSIC	2	949659	49555	509			3.71	135.7	2.23	132.7	1.85	n.d.						
	IMO	3	959548	39890	430			1.07	41.2	1.56	87.5	0.79	n.d.						
	CIVISA	4	952248	47051	509	1.49	0.83		72.1	1.98	114.2	1.31	n.d.						
	IPGP - OVSG	5	957669	41705	439	1.31	4.08		86.7	1.63	92.1	1.00	n.d.						
INGV - OV	INGV - Pa	6	953664	45847	300	1.52	0.00		73.5	2.19	110.7	0.58	1.84	439	-3.34			-4.19	32.18
	IGN - CSIC	7	949981	49435	324	2.32	0.66		115.7	2.70	137.5	0.74	9.13	375	-3.95			-4.04	29.18
	IMO	8	956507	43054	289	1.05	0.00		51.6	1.96	94.4	0.50	n.d.	408	-2.93				
	CIVISA	9	945160	54249	352	2.22	0.18		108.3	2.35	125.0	0.64	0.66	371	-4.19			-4.09	29.32
	IPGP - OVSG	10	955363	42636	278	17.18	204.88		1392.4	1.85	106.3	0.59	0.58	298	-0.08	-31.4	-5.82	-3.97	29.04
INGV - Pa	INGV - Pa	11	951055	48289	301			8.72	236.0	1.93	108.8	0.49	0.023			-33	-6.5	-4.12	
	IGN - CSIC	12	958262	41328	250			1.08	61.3	1.78	95.8	0.42	0.015					-4.23	
	IMO	13	955386	44204	276			2.56	54.0	1.36	76.0	0.31	0.009						
	CIVISA	14	954802	44774	278			0.03	47.4	1.64	96.9	0.42	0.012					-4.08	
	IPGP - OVSG	15	951109	47092	288			243.55	1165.5	1.71	99.7	0.42	0.027			-36	-6.7	-4.02	
IPGP - OVSG	INGV - Pa	16	949458	50031	311	1.53	0.19		64.6	1.37	130.8	0.43	0.72						
	IGN - CSIC	17	953150	46427	253	1.60	0.12		68.6	1.02	98.3	0.33	0.52						
	IMO	18	940741	58731	352	1.11	0.70		47.1	1.33	125.1	0.41	0.71						
	CIVISA	19	889796	109251	597	3.60	3.69		153.0	2.08	191.8	0.69	1.08						
	IPGP - OVSG	20	940833	58593	358	1.85	0.68		85.2	1.34	126.1	0.41	0.71						

When data was shared some teams advised on specific technical problems encountered, mainly:

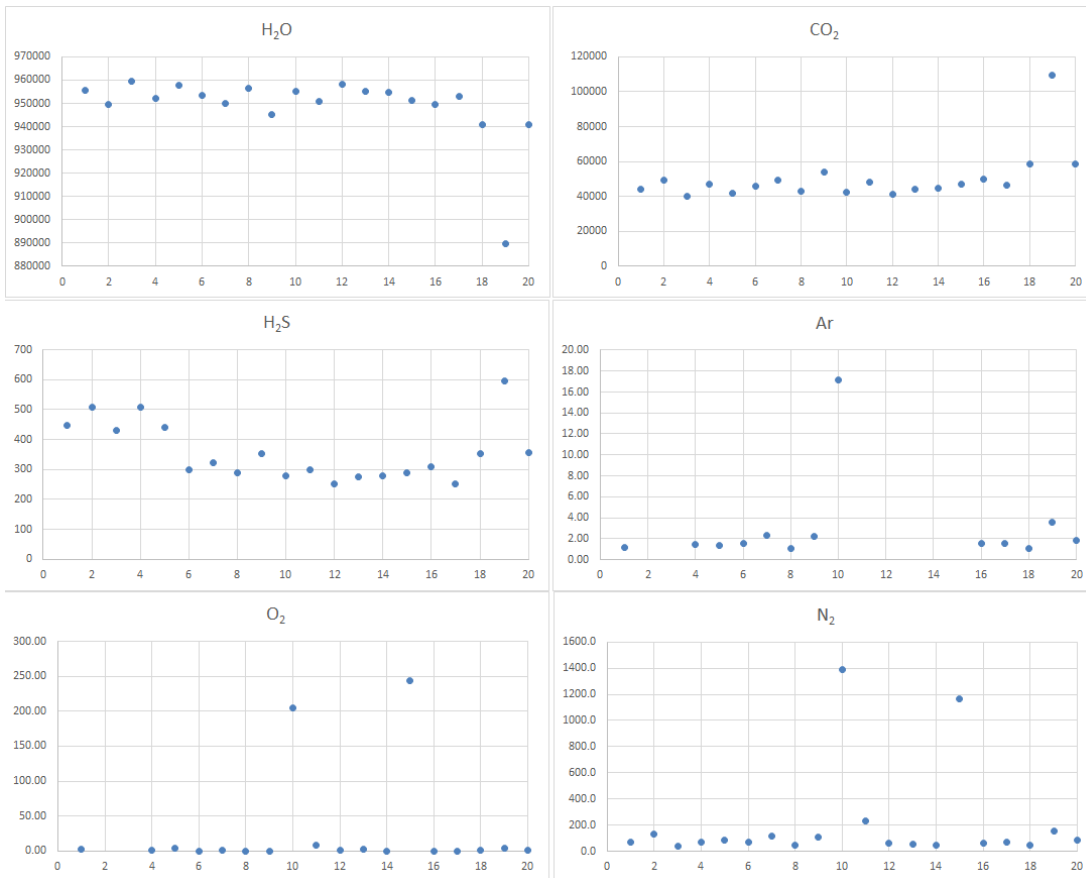
- CIVISA informed about a problem with the H₂S detection. This team understood a posteriori that they had a titrant problem;
- Sample collected by IGN-CSIC and analysed by CIVISA was identified in the shared file as evidence of flux problems during sampling;
- INGV-OV informed that the dry gas sample collected by IGN-CSIC showed evidence of being air contaminated and thus the CO concentration of this sample could not be feasible. In addition, the dry gas sample collected by INGV-Pa was “wet” with possible interference (increase) of the analysed element.

Descriptive statistics (Table 7) were calculated and graphics were plotted to analyse the dispersion of the different analysed gas species (Fig. 2). Considering the few available data, and the fact that at least two samples (Ref. 10 and 15, Table 6) showed clear air-contamination as agreed by all the teams, the consortium partners concluded that any statistical treatment of the data should be done prudently and all results used carefully. Still, and considering that the IPGP-OVSG and CIVISA teams produced two reports to try to evaluate the data, some suggestions for future studies will be given. Regarding isotopic data, and taking into account that very few data are available, the analytical results are included in Table 6, but no further statistical analysis was made.

Table 7. Descriptive statistics of the Furnas Volcano results (all data included) (RSD – relative standard deviation).

Parameters	H ₂ O (ppm)	CO ₂ (ppm)	H ₂ S (ppm)	Ar (ppm)	O ₂ (ppm)	Ar+O ₂ (ppm)	N ₂ (ppm)	CH ₄ (ppm)	H ₂ (ppm)	He (ppm)	CO (ppm)
<i>n</i>	20	20	20	13	13	7	20	20	20	20	14
Average	948991	50304	357	2.92	16.86	37.25	206	1.80	113	0.67	1.15
Median	952699	46739	317	1.53	0.68	2.56	73	1.82	109	0.54	0.62
Standard Deviation	14867	14822	99	4.34	56.51	91.02	371	0.41	25	0.39	2.36
RSD	0.02	0.29	0.28	1.49	3.35	2.44	1.80	0.23	0.22	0.57	2.06

One of the aspects under discussion by the partners was the removal of “gross errors”, clearly due to anomalous sampling/storage conditions (e.g., air-contaminated samples), prior to any statistical treatment. In the context of a volcano observatory, or any other use of the data, there was consensus that samples 10 and 15 should be removed due to the high concentration of atmospheric gas species (Ar, O₂, N₂). When these air-contaminated samples are removed, the relative standard deviation (RSD) of some of the above-mentioned gas species improved (Table 8). CO also showed high variability compared to the other analysed elements, but after removing the data previously identified as having technical issues, the RSD improved.



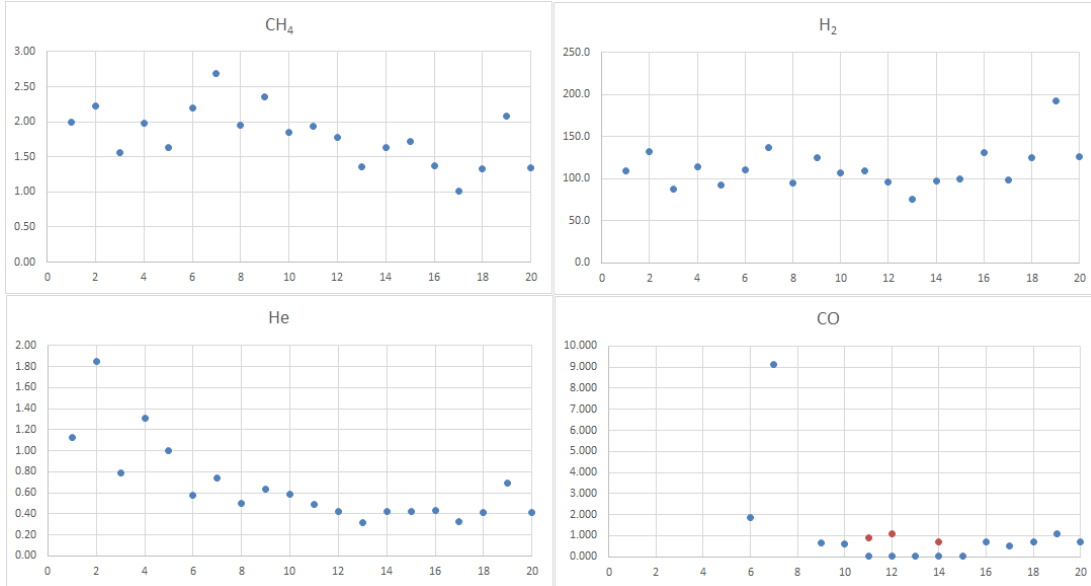


Figure 2 – Plots of the gas species analysed (all results included). For the case of CO, red dots in analysis 11 to 14, correspond to the data analysed by INGV-Pa in the dry phase.

There are two additional samples that some partners considered air-contaminated (ref. 11 and 19) and for this reason, they were left for further analysis.

Table 8. Descriptive statistics of the gas data after removing the samples identified as 10 and 15 (RSD – relative standard deviation).

Parameters	H ₂ O (ppm)	CO ₂ (ppm)	H ₂ S (ppm)	Ar (ppm)	O ₂ (ppm)	Ar+O ₂ (ppm)	N ₂ (ppm)	CH ₄ (ppm)	H ₂ (ppm)	He (ppm)	CO (ppm)
<i>n</i>	18	18	18	12	12	6	18	18	18	18	12
Average	948520	50908	365	1.73	1.19	2.86	87	1.80	114	0.69	1.29
Median	952699	46739	338	1.53	0.67	1.82	70	1.85	110	0.54	0.68
Standard Deviation	15625	15527	101	0.71	1.51	3.15	49	0.43	26	0.40	2.53
RSD	0.02	0.30	0.28	0.41	1.27	1.10	0.56	0.24	0.23	0.58	1.97

Different teams analysed the resulting datasets based on distinct approaches: (i) the concentration of the single species, (ii) gas ratios or even (iii) based on normalization of the variables. Previous studies (Giggenbach and Matsuo, 1991; Giggenbach *et al.*, 2001) used normalized data to evaluate dispersion and differences between the gas species. This normalization procedure is aimed at avoiding secondary processes associated with condensation during sampling. In this case, normalization of gas contents to H₂O was carried out, and then the composition of the dry species was normalized to CO₂, the major component in the dry gas phase. Final values were normalized to the median. Dispersion of the data based on this last approach is shown in Figure 3, as was done previously in the literature with similar aims.

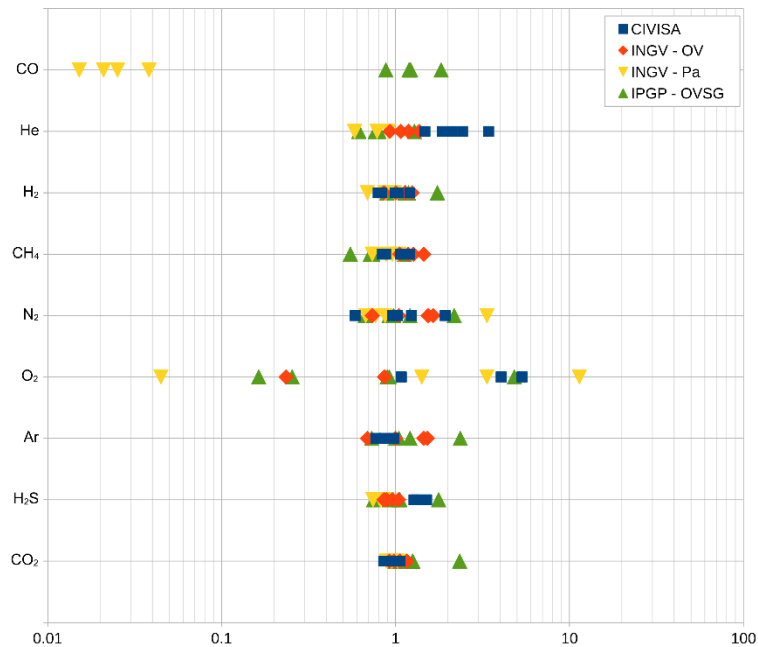


Figure 3. Dispersion of the normalized data around the median of the results from Furnas Volcano joint survey (after removing the two air-contaminated samples). Only results from the soda bottles are displayed, CO data from INGV-OV are not displayed in the figure as the analysis was carried out in the dry bottle.

Several gas ratios obtained from the composition of fumaroles are used in the literature for volcano monitoring, for geothermobarometry and even to establish comparisons with data measured by other techniques (e.g., MULTIGAS). All partners agree that plotting the ratios in diagrams or graphics gives valuable information about the data and contributes to estimating the geothermobarometers. The most used gas ratios are $\text{H}_2\text{O}/\text{CO}_2$, CO_2/CH_4 , H_2/CH_4 , Ar/H_2 , CO/CO_2 , CO/CH_4 , He/CO_2 , H_2/Ar , $\text{H}_2\text{S}/\text{CO}_2$, $\text{He}/\text{H}_2\text{O}$, $\text{H}_2/\text{H}_2\text{O}$, N_2/Ar (e.g., Aiuppa *et al.*, 2017; Caliro *et al.*, 2007; 2011; Chiodini, 2009; Chiodini and Marini, 1998; Fischer *et al.*, 2015; Ohba *et al.*, 2019; Tassi *et al.*, 2017).

Nevertheless, if the aim is to compare the precision and accuracy of results from each laboratory, the use of ratios is probably not the most adequate approach to gain understanding of the reason for the variability of each one of the gas species, or even to apply parametric statistical tests to understand the variability associated with the methodology. In fact, the application of statistical tests to the gas ratios may be questionable and challenging as it includes variability of two “independent” variables, resulting in datasets that usually do not follow the required statistical assumptions, such as normal distribution.

As previously mentioned, some statistical tests of the acquired data were applied by two different teams, IPGP-OVSG and CIVISA. The IPGP-OVSG team suggested using Grubbs and Cochran tests to evaluate the average and variability between the different laboratories (as mentioned in the ISO5725 standard procedure). IPGP-OVSG also suggested the Dixon test to evaluate the presence of outliers in the datasets. The Dixon test is used for small datasets ($n \leq 30$), which seems appropriate for the current study case. However, the difficulty in applying these tests persists because they are parametric approaches, requiring the datasets to be normally distributed. This aspect was a point of some debate between the consortium teams. IPGP-OVSG argued that they used the robustness of the Dixon test because if there is an outlier in the data set, then the outlier will likely cause the normality test to show non-normality. According to IPGP-OVSG, focusing on non-normality of the dataset is a minor issue, although not unimportant. While the Dixon test involves an assumption of normality, it is both good at

detecting outliers and is robust in detecting departures from normality. In particular, as mentioned by Chernick (1982), the test seems to maintain significance level even when the distribution is very non-normal (*i.e.*, uniform, exponential, such as for a small data sets). On the other hand, checking and subsequently rejecting the normality assumption based on preliminary application of the non-parametric Kolmogorov-Smirnov or the Shapiro-Wilk tests to the datasets led the CIVISA team to propose that only for the variables that follow a normal distribution should the above-mentioned Grubbs and Cochran tests be applied. Besides, CIVISA suggested the use of quartiles when data did not follow a normal distribution. By applying these tests, further outliers were identified. Again, and as mentioned at the beginning of this sub-section, the small amount of data acquired is not adequate for a robust statistical treatment of the data, but the aim is to identify some of the possibilities that can be used in future studies.

In spite of the agreement on the statistical methodological approach, the controversy stands partially unsolved about the acceptance or the rejection of the assumption of (expected) normality in the data distribution. All partners agreed that the whole discussion would benefit from a much larger dataset, given the validity of the central limit theorem.

2.1.3) Additional intra-laboratorial testing

As mentioned earlier, the partners recognized that the variability associated with the joint survey could be caused by several uncontrolled variables. In order to try to identify some of the factors that might be interfering with the results, the partners decided during a web meeting in May 2020, to carry out additional tests in an intra-laboratorial context, as it was impossible to perform a second joint field survey due to the pandemic limitations.

The tests were carried out by the CIVISA and IPGP-OVSG teams and were aimed at:

- Evaluating the impact of different amounts of soda in the bottles (controlling the volume of the headspace);
- Checking the effect of time duration between sampling and analysis of the gases collected.

A third partner (INGV-Pa) was not able to participate since the sites devoted to the survey at Vulcano Island (Aeolian archipelago) were not accessible.

Two surveys (July and September 2020) were carried out by the CIVISA team to check the effects of soda amount on the analysis, where the bottles were filled at 20%, 40% and 60% of total volume of the flasks with the usually used basic solution (NaOH, 4M). Two bottles were filled with the volume of soda solution used in the observatory in routine analysis and corresponding to about 40% - 45% of the volume of the bottle (it is not quantified with precision). Gases were collected with the same type Giggenbach bottles, using the same sampling line and the same operator carrying out the sampling. The IPGP-OVSG team performed a similar survey in August 2020, where the time span between sampling and analysis was also tested. Sampling time was registered, since it was not the same for all the samples. From the surveys, fourteen and six analyses, respectively, from CIVISA and IPGP-OVSG are available resulting from tests on the effect of the soda amount (Table 9).

Previous to these tests, in January 2020 CIVISA performed another survey always at the same testing site (Caldeira Seca, at Furnas Volcano) to evaluate the effects of the time between sampling and the analyses, resulting in four additional gas analyses (Table 10).

Figures 4 and 5 show the results for the volume of basic solution, respectively from CIVISA and IPGP-OVSG, and Figure 6 shows the results related to the time between sampling and analysis carried out by CIVISA.

Table 9. Chemical analysis of the gases collected by CIVISA and IPGP-OVSG to test the effects of different filled volumes in the Giggenbach bottles, as well as the effect of time span between sampling and analysis in the IPGP-OVSG case.

Volcano	Date	Team	Filled volume of basic solution (%)	Temperature (°C)	ppm											Sampling time (min)	Condensate weight (g)	Time span between sampling and analysis (days)
					O ₂ +Ar	Ar	O ₂	N ₂	CH ₄	He	H ₂	CO	CO ₂	H ₂ S	H ₂ O			
Furnas	08/07/2020	CIVISA	-	96.8	4.50	-	-	56.83	1.77	1.33	99.89	n.d.	42906	245	956685	13	42.118	1
Furnas	24/09/2020	CIVISA	-	96.9	1.38	-	-	49.40	1.76	1.07	101.48	n.d.	43046	263	956536	8	57.584	6
Furnas	08/07/2020	CIVISA	20	96.8	12.45	-	-	71.27	1.69	1.66	103.87	n.d.	46197	284	953328	16	28.772	1
Furnas	08/07/2020	CIVISA	20	96.8	6.37	-	-	45.31	1.56	1.30	93.09	n.d.	41623	237	957993	7	36.641	1
Furnas	24/09/2020	CIVISA	20	96.9	4.25	-	-	54.39	2.41	1.86	106.43	n.d.	45749	267	953815	6	28.668	6
Furnas	24/09/2020	CIVISA	20	96.9	5.62	-	-	61.35	1.92	2.05	111.06	n.d.	48480	282	951056	8	28.688	6
Furnas	08/07/2020	CIVISA	40	96.8	1.97	-	-	50.33	1.59	1.00	91.30	n.d.	43336	261	956257	16	49.203	1
Furnas	08/07/2020	CIVISA	40	96.8	1.08	-	-	50.61	1.66	0.92	97.20	n.d.	42779	264	956805	17	57.058	1
Furnas	24/09/2020	CIVISA	40	96.9	1.78	-	-	54.89	1.81	1.10	109.60	n.d.	47533	283	952015	12	50.015	6
Furnas	24/09/2020	CIVISA	40	96.9	1.15	-	-	36.33	1.50	0.93	86.19	n.d.	43293	263	956318	8	56.74	6
Furnas	08/07/2020	CIVISA	60	96.8	1.11	-	-	35.81	1.36	0.76	77.27	n.d.	38077	223	961584	9	42.713	1
Furnas	08/07/2020	CIVISA	60	96.8	1.60	-	-	53.46	1.96	0.93	107.73	n.d.	47549	277	952009	12	47.494	1
Furnas	24/09/2020	CIVISA	60	96.9	1.46	-	-	46.17	1.64	0.84	89.63	n.d.	48291	288	951281	15	49.528	6
Furnas	24/09/2020	CIVISA	60	96.9	1.54	-	-	52.86	1.81	0.92	103.62	n.d.	48487	288	951064	13	40.338	6
La Soufrière	05/08/2020	IPGP-OVSG	20	-	11.83	1.00	10.83	114.91	0.22	0.13	31.89	0.153	21234	4478	974129	34	-	1
La Soufrière	05/08/2020	IPGP-OVSG	20	-	11.43	1.00	10.42	118.67	0.22	0.13	33.44	0.148	21377	4667	973792	33	-	1
La Soufrière	05/08/2020	IPGP-OVSG	40	-	1.20	0.96	0.24	114.79	0.21	0.13	32.86	0.128	21208	4377	974266	21	-	2
La Soufrière	05/08/2020	IPGP-OVSG	40	-	1.48	0.95	0.53	120.57	0.24	0.14	35.42	0.141	24822	4601	970420	23	-	2
La Soufrière	05/08/2020	IPGP-OVSG	60	-	0.88	0.83	0.05	104.51	0.19	0.12	29.43	0.107	27275	4064	968525	10	-	5
La Soufrière	05/08/2020	IPGP-OVSG	60	-	1.16	0.93	0.23	121.04	0.24	0.13	35.60	0.108	33877	4596	961369	15	-	5

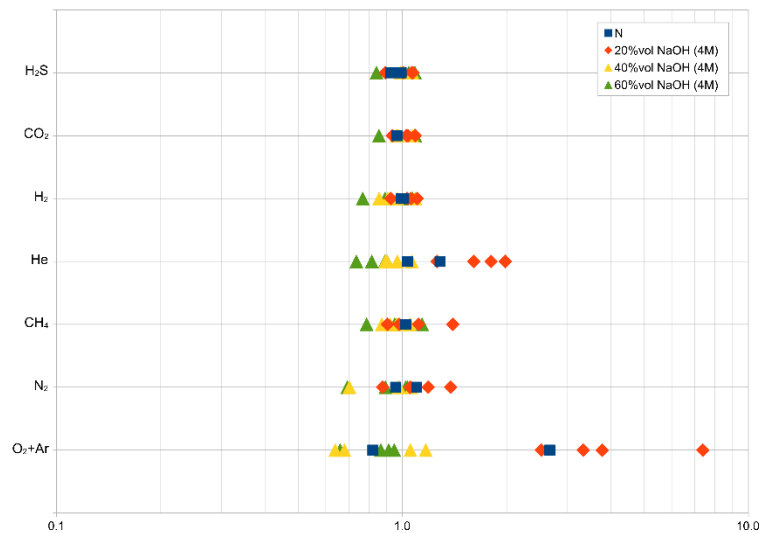


Figure 4. Dispersion of the normalized data around the median for the tests related to soda volumes (data from surveys carried out by CIVISA in July and September 2020). “N” refers to the amount of basic solution routinely used in the observatory analysis and 20%, 40% and 60% refer to the volume of soda (NaOH 4M) filling each bottle.

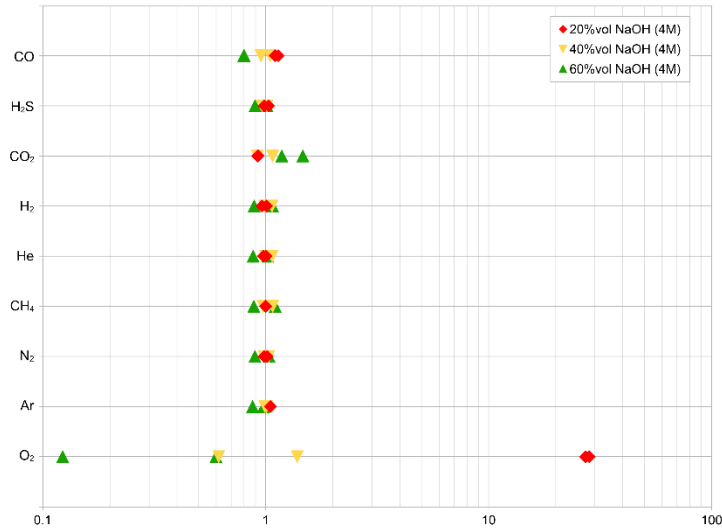


Figure 5. Dispersion of the normalized data around the median for the tests related to soda volumes (data from surveys carried out by IPGP-OVSG team in August 2020).

Table 10. Chemical analysis of the gases collected by the CIVISA team in January 2020 to test the time span between sampling and analysis.

Volcano	Team	Temperature (°C)	Sampling Date	Analysis Date	Time span between sampling and analysis (days)	ppm								Sampling time (min)	Condensate weight (g)
						O ₂ +Ar	N ₂	CH ₄	He	H ₂	CO ₂	H ₂ S	H ₂ O		
Furnas	CIVISA	98.8	16-01-2020	20/01/2020	4	1.65	58.50	1.72	0.92	98.23	42462	273	957104	11	58.665
Furnas	CIVISA	98.8	16-01-2020	20/01/2020	4	1.27	50.36	1.70	0.77	94.24	44280	276	955296	10	59.392
Furnas	CIVISA	98.8	16-01-2020	06/02/2020	21	1.56	63.47	1.83	0.89	102.91	40270	267	959292	13	59.648
Furnas	CIVISA	98.8	16-01-2020	13/02/2020	28	2.55	95.86	2.06	1.29	121.43	46622	265	952890	16	43.545

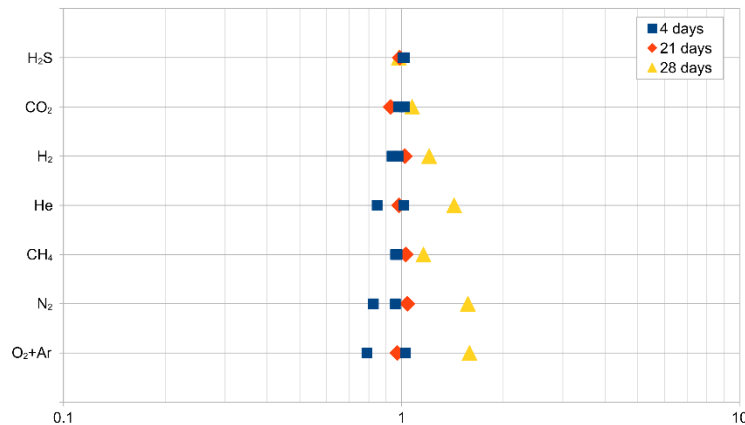


Figure 6. Dispersion of the normalized data around the median for the test carried out by CIVISA in January 2020 to check the effect of time span between sampling and analyses of the data.

Despite sampling different fumaroles (with specific temperature, compositions, fluxes, geological setting et c.), results obtained independently by the two teams highlight that gas analysis associated with 20% volume of soda show higher variability (Fig. 4 and 5). In the case of CIVISA, higher variability also seems to be observed for the gases analysed in the headspace (H₂, He, CH₄, N₂, O₂, Ar). IPGP-OVSG also showed higher O₂ content for the 20% soda volume, similar to CIVISA for the sum O₂+Ar. Even if the amount of data available is small, higher variability is also observed for the samples analysed after 28 days compared to the data analysed in the first 21 days (Fig. 6).

All the above described activities carried out in the EUROVOLC project form the basis for the development of best practices specifically focused on the type of fumarolic emissions sampled. In addition, and considering the significant number of factors that may interfere with this methodology, best practices essentially aim at contributing to the definition of some common strategies that may be useful for the different laboratories.

3) Recommendations for “best practices in direct gas sampling”

As mentioned above several factors may affect the gas sampling and/or analytical procedures, thus resulting in variability of the data. Our goal was to contribute to identifying possible factors that may interfere with the results and to suggest some common strategies that may potentially contribute to improving the overall application of this methodological approach. The suggestions will not only be relevant for the laboratories that are already developing this type of gas sampling and analysis, but also for potential partners that aim to start this line of research.

There is not a single “recipe” for the application of this methodology and the selection of procedures is highly site dependent, essentially regarding the type and temperature of the gas emission. The recommendations presented here result from the activities carried out during the EUROVOLC project, namely the joint and intra-team surveys carried out, as well as from the several years of experience of the consortium teams. Data from the literature also support some of the recommendations on direct sampling in fumaroles with the so-called Giggenbach methodology.

The consortium teams agree that differences in the application of this methodology may derive from the different phases, from the pre-sampling preparation to the data analysis. Thus, the recommendations account for these different steps.

A general suggestion is that teams should have protocols for preparation, sampling and analytical procedures of the gases collected in fumaroles. The protocols would be a guide, not only for the teams that routinely sample the fumaroles and that can check if all the material is available (as for instance, using checklists), but also for future new researchers to follow similar procedures.

3.1) Pre-Sampling preparation

Preparation of the sampling is of major importance and may control the success of the survey. The selection of the sampling material, as well as the preparation of the gas bottles are essential for the results obtained and the data quality.

Some recommendations for this pre-sampling phase is the importance of:

- *Checklists*
- *Protocols* for the procedures of gas bottle preparation, sampling or even application of the analytical techniques.

Based on the partners' experience, we list the material that commonly is part of the checklist associated with the "material to bring to the field":

a) Checklist for the sampling material:

- Giggenbach bottles filled with NaOH 4M solution, pre-evacuated and weighted
- Gas bottles (for eventual complementary sampling of dry gas)
- Plastic flasks (for acid condensate)
- Funnel or probe with silicon pipes, dewar tubes (if it is the case)
- Thermocouple and probe
- Latex gloves
- Thermal gloves
- Disposable protective material, including protection overall, gas masks and filters
- Small shovel
- 20 mL syringe fill with Milli-Q water
- Parafilm paper
- Squeeze bottle with Milli-Q water
- Batteries for the thermocouple
- Condenser (for eventual sampling of dry gas)
- Battery circuit to pump water for the condenser (for eventual sampling of dry gas)
- Switchblade
- Screwdriver
- Three ways stopcock with 100 ml plastic syringe.
- Bucket
- Safety glasses
- Field notebook
- Digital watch (or any device to control the time)

Each team will have specific checklists, even depending on the type of gas emission. Still, the recommendation is to have the checklist in order to avoid lack of material in the field that can compromise the entire survey.

b) Preparation of the Giggenbach gas bottles with soda solution:

The Giggenbach bottles are prepared in the laboratory and this procedure may occur several days before sampling. Depending on the number of bottles to prepare, or even whether the fieldwork will occur far from the laboratory facilities, the time between preparation of gas bottles and sampling may span from one day to more than one week. Our recommendation is that the time span between preparation and sampling should be as short as possible. In this framework, one of the most important aspects is the warranty that the stopcocks are efficient to avoid leaking. One of the major issues in any sampling strategy is avoid the presence of air contamination that can interfere with the results and constitute "gross errors". For this reason, the type of stopcock and a good vacuum of the gas bottle are crucial.

Some aspects to consider:

- *Use of KOH vs. NaOH basic solution.* Most of the literature shows that the majority of teams use NaOH (4 M) as the soda solution to prepare the Giggenbach bottle. There are some examples of the use

of KOH (12 M) for some cases when the CO₂ amount was very high, nevertheless, most of the teams use the NaOH basic solution, which even for safety reasons is eventually more advisable than the higher concentration associated with the KOH solution. The existence of potential differences was not tested in the current project, but in the past some research groups used KOH and results should be comparable.

- *The volume of soda sample in the gas bottle* may be another aspect to consider. The tests carried out in the project showed that soda filling only 20% of the bottle volume would result in a higher O₂ amount in the Giggenbach bottles. This observation suggests that bottles should be filled with higher volume of soda sample, and the teams suggest a value around 40% volume of the gas bottle as an adequate approach. This amount of basic solution seems to accomplish with the binary data quality and sampling time.

- *Gas bottles (dimension, volume) and stopcocks* may be different between teams and even the same team may have different material. The most relevant aspect to consider is the warranty of no air contamination in the sample before, during or after sampling. To achieve this, the type of stopcocks is crucial and they should have O-rings so that vacuum conditions are kept both before the sampling and during storage to prevent air contamination in the bottle. The volume of the gas bottles may be a relevant aspect for the time of sampling. Higher dimension gas bottles usually correspond to longer sampling time and this can be a criterion for deciding what material will be used. A compromise between the amount of collected gas and sampling time is needed, especially when sampling is carried out in acidic environments that may cause safety problems to the researchers. The different gas bottles used in the tests (volume from about 150 ml to 1000 ml, one or two stopcocks made by different manufacturers) carried out during the EUROVOLC project do not seem to be a major contributor to the final variability. Nevertheless, if possible, teams should use the same type and volume of gas bottle (and stopcocks) within the same survey.

- *Vacuum pump*. Teams use different vacuum pumps and the most important aspect is that the pump needs to be efficient to perform an adequate vacuum and removal of any air from the sample. A rotary vane pump as that one used at the CIVISA laboratory for the surveys is an adequate pump to accomplish this goal, since it is robust, requires low and cheap maintenance and is efficient enough to remove the air from the Giggenbach bottles.

- *Analytical balance*. Teams also use different balances, and a precision of at least 0.001 would be required. Periodic calibration of the instrument is recommended since an incorrect weight can compromise the results.

b.1) Checklist for preparation of the gas bottles. This is an example of checklist since some differences may occur between laboratories (material needed for preparation of the basic solution and for filling the gas bottles):

- Sodium Hydroxide (NaOH) pellets (purity: 99%)
- Milli-Q water (Ultrapure, type 1)
- Sampling bottles (Giggenbach type)
- Rubber caps to seal side entry of bottles
- Kitasato
- 600 mL and 1 L beakers
- Spatula

- Glass stirring rod
- 20 mL syringe
- Universal support and grapple
- Rotary vane pump
- Heating plate
- Analytical balance

3.2) Sampling

Together with the natural variability of the fumarole during sampling, several factors may interfere in this phase, such as the human factor (experience in sampling and in selecting the site), the different apparatus and sampling line, or the sampling time, just to give some examples.

a) Selection of the sampling site

Selection of the sampling site is a major aspect and relies on the experience of the researchers with both the type of fumarole and the sampling site. It is advisable, if possible, that at least one experienced individual in sampling fumaroles will be in the field as part of the research team.

- *The selected sampling site* should be the best representative of the gas emissions from depth. Usually it corresponds to high flux zones and to the higher temperature spots. Researchers need to avoid possible sources of air contamination, so the site needs to be well sealed. This is particularly challenging in some low temperature/flux fumaroles. In some cases, mainly in high temperature environments, safety aspects also control the selection of the sampling site. When the research team routinely uses the same sampling site, as for instance for regular volcano monitoring activities, this step is usually overpassed and in some cases, a probe may even be permanently installed in the fumarole. However, when the site is unknown and the team never sampled the area, a temperature survey is advisable as well as evaluation of the fluxes in order to select the most appropriate site.

- *Metadata*. During sampling, all the relevant information should be written in a notebook or on some forms previously prepared with the main information that can be relevant to understand the results.

Some of the main metadata that should be added on the forms are:

- Location (coordinates of the sampling site)
- Volcanic system
- Fumarole type
- Type of sampling line
- Operator
- Time and duration of sampling
- Additional observations that can help to understand the results (*e.g.*, reduction of flux during sampling, condensation of water in the line)
- Take pictures or videos (if possible) that can be useful for future understanding of the field conditions.

b) Sampling apparatus

The selection of the material to sample the fumaroles may be highly dependent on the sampling site and is usually chosen in the pre-sampling operations, when researchers already know the sampling site.

- *Use of a funnel or a probe inserted in the soil* is a relevant aspect to consider and depends on the characteristics of the sampling site, which needs to be evaluated by each team. The insertion of a probe in the soil is the method most described in the literature and frequently used by the majority of the consortium teams. However, when there is presence of boiling water at a shallow depth, the use of a funnel is advisable, and the funnel needs to be isolated from the outside environment to prevent atmospheric contamination. The latter is the particular case for Furnas fumaroles and in the Azores in general. The use of funnel is also mandatory to sample submarine fumarolic emissions. As better described in the next section, the selection of the material used for the funnel and the probe, strongly depends on the temperature of the gas emission. Plastic funnels can be used for fumaroles with a vent temperature around the boiling point. For higher temperatures, stainless steel is highly recommended due to its robustness, resistance and low reactivity to magmatic gases.

- *Material on the sampling line (probe, tubes)*. The selection of the material used in the sampling line depends on the temperature of the gas emission. The most common material used in the probes is stainless steel and for the higher temperature fumaroles (> 600 °C) titanium tubes are advised. For some very high temperature cases, quartz tubes are used. Iron probes are not advisable as iron may react with water and form H₂. The tubes used for sampling may also be of different material (silicon, dewar tubes) depending on the temperature of the sampling site.

3.3) Analytical procedures

Laboratories may use different techniques to analyse the gases collected from the fumaroles. The analytical procedures are even different depending on the gas species that are under analysis. Table 3 shows the different techniques usually used to analyse the gas species by the consortium teams.

Despite the different techniques used, the research teams implement some general strategies:

- *Use of standards*. All laboratories use standards to calibrate the instruments and to be able to quantify the analysed species. However, distinct standard concentrations are used, as expected, and depending on the average composition of the samples that are routinely analysed by each team (for details, Table 4).

- *Protocols*. We recommend laboratories to have protocols with the description of the analytical methodologies, standard and calibration procedures. A list of the material used, including the technical characteristics of the instruments is suggested. Sharing of these protocols and technical characteristics of the instruments between teams could contribute not only to highlight some differences between teams, but also to help new teams to set up this type of analytical methodology.

- *Metadata*. Despite information about the technical procedures and instruments used, some additional information should be added as metadata to support the results:

- Laboratory technician responsible for the analysis

- Name of the individual responsible for the laboratory (and who should check the results)
 - Instruments used (type, model)
 - Analytical dates (may be different considering the techniques used)
 - Standards used
 - Any observation that can be useful to understand the results
- *Time span between sampling and analysis of the collected gases.* Even considering that the use of adequate stopcocks would prevent the leaking of gases from the Giggenbach bottle, some of the gas species may react with each other and/or with the basic solution and, therefore the analysed composition may change over time. The time span between sampling and analysis was not carefully tested in the current project, however, the more advisable strategy is to analyse the gases collected as fast as possible, and potentially the time span should be less than 1 month.
- *Evaluation of the intra-laboratory variability for each gas species* (accuracy and precision of the results) by the different laboratories is a relevant aspect before setting up inter-laboratory calibration strategies and comparison with other laboratories. Variability and uncertainty strategies, as well as quantification of the limits of detection of each species, may be challenging and sharing of experiences between teams is welcome.
- *Existence of pre-defined automatic forms* to add the data and routinely obtain the total chemical analysis is crucial to avoid human errors in the insertion of data or estimation of the different parameters. We recommend, however, a careful review of the worksheets by at least two members of the teams in order to avoid systematic errors. An additional recommendation could be to request a member from another laboratory to review the defined forms in order to evaluate potential calculation problems.
- *Inter-laboratory calibration procedures* between laboratories allow comparison of data obtained between different teams. In order to accomplish this goal together with the setup of joint surveys, a common laboratory standard shared by different teams is suggested. The consortium teams will implement such a strategy in the following months by sharing, between the laboratories identified in Table 3, at least one gas with known standard composition and collected in the Giggenbach bottle. Following this procedure, the aim is to simulate as much as possible the sampling of a fumarole. Several variables will be controlled, such as the use of similar bottles and stopcocks, same soda solution and soda volume, similar sampling time and operator. The results will be shared on a common day following the suggestions for blind sharing and evaluation of results.
- *Importance of having a permanent individuals responsible for the laboratory* and for the control of the data. Double checking of the final datasets is crucial to avoid eventual typos on the data.

a) **Checklist for some laboratorial material (common to the different partners)**

- Depending on the technique applied by each laboratory, different supporting materials are needed, however, some common materials are listed below, such as:
 - Pressure gauge
 - Rotary vane pump
 - Gas standards (different concentration mixtures depending on the sampling site)
 - Analytical balance
 - Reactants

3.4) Data analysis

Application of potential statistical tests to the data obtained, or even plotting the data in pre-defined diagrams, are some of the possibilities associated with the data analysis and depend on the aim of the team. Even though, all teams agree that after obtaining the results, cleaning the datasets from the “gross errors” is mandatory, essentially regarding the presence of air-contaminated samples or any other reported technical aspect.

- *Double check of the data before further data treatment or sharing of the results.* Before any application of mathematical approaches to the data, two operators should review the dataset to identify potential typos. As we mentioned above, it is recommended to use automatic worksheets that can be filled during the laboratorial procedures. However, a double check is suggested before any further analysis.

- *Identification of air-contaminated samples.* Air-contaminated samples are usually identified based on the amount of atmospheric species (O_2 , N_2) or in the ratio N_2/Ar , for instance. If the Ar isotopes are available for the analyses, they give clear information about the presence of atmospheric air in the sample, however only a few laboratories are able to perform these analyses (only INGV-OV among the consortium partners). In some cases, the observations written in the field (*e.g.*, sampling time deeply different for two identical Giggenbach bottles) or in the laboratory (*e.g.*, injection pressure higher than expected) also support excluding some data due to technical problems or evident malfunctioning.

- *Identification of outliers.* Recognition of “anomalous” data may be relevant not only to associate with potential technical problems, but they can also represent opportunities to identify changes in the system. Commonly, statistical tests are useful to identify possible outliers but they require not only a significant number of data but also certain assumptions (as for example, the normality). Based on the ISO5725 standard procedure and the experience of some partners, a list of potential statistical tests includes:

- Dixon test ($n \leq 30$) requires normal distribution. Useful to detect outliers;
- Quartiles test (when datasets do not follow the normal distribution).

- *Inter-laboratory calibration tests.* Based on the ISO5725 standard procedure, two tests are suggested to evaluate differences in the average and variability of the results obtained by the distinct laboratories:

- o Grubbs test (requires normal distribution) – aims to identify differences in data obtained by different laboratories.
- o Cochran test (requires normal distribution) – aims to evaluate inter-laboratorial variability.

Before applying any parametric statistical test, requested assumptions need to be checked. For instance, for the normality there are several non-parametric tests available and the significance should be at least 95%. When application of the above-mentioned tests is not possible due to lack of normality, we recommend the use of a quartiles test as a possibility.

- *Blind evaluation of the datasets* is suggested when inter-laboratorial calibration is carried out. Data should be shared at the same time (sent to one person all at the same time). Two possibilities in this case: that person would reclassify the samples and share them with all the partners to allow a blind evaluation of the data, or, as a second option, the reclassified samples would be sent to an external person that would make an evaluation of the data.

Main Considerations

Direct sampling of fumaroles is challenging, and several factors may interfere with the final variability observed in the resulting datasets. Sampling using the so-called Giggenbach methodology is time consuming and requires a laboratory with several types of equipment and skills in order to obtain a complete chemical analysis of the gas sampled. Nevertheless, the volcanological community recognizes that this persists as the more accurate and complete technique to characterize gases emitted in fumaroles, including low and high temperature emissions.

Together with the natural variability of the sampling site, differences in the final data may result from the sampling, the analytical procedures or even the data treatment. For this reason, understanding and identifying the intra-variability of each laboratory is essential, followed by inter-laboratory calibration tests carried out between the involved research teams. The application of standard strategies between the different teams is relevant and the test of common gas standards constitutes a potential strategy to understand some of the potential variability observed between the teams.

Even if differences are observed between laboratories, common strategies may help to accomplish best procedures namely:

- *Implement checklists*
- *Create protocols*
- *Implement routine use of metadata (in the field and laboratory) that should be added to the final database*
- *Use automatic forms to fill in all the information (weights, time of sampling, concentrations, pressure,...)*
- *Evaluate intra-laboratory variability for the different gas species*
- *Implement inter-laboratory calibration strategies with other laboratories*
- *Ask for help and collaboration with other more experienced teams*

This type of European network has strongly contributed at the community building and opened possibilities to maintain and strengthen collaborations even after the end of the project. Extending the invitation to other teams, with or without experience, who are not involved in EUROVOLC is also a common goal and may contribute to improving the methodologies developed by each team. Further joint surveys in different fumarolic fields with different characteristics (temperature, flux, composition, geological settings,...) would be welcome to implement the best practice in other case studies and would allow sharing of experiences and improvement between the teams.

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