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Sulfur Species in Volcanic Gases

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A new analytical method for the determination of the sulfur species (SO₂, H₂S, S₈⁰) in volcanic gases is proposed by revising, updating, and improving previous methods. The most significant advantages of the proposed procedure can briefly be summarized, as follows: (i) the reaction among sulfur species stops during the gas sampling by using preevacuated thorion-tapped vials with purified 0.15M Cd(OH)₂ in 4 M NaOH to favor the precipitation of H₂S as CdS; (ii) all the sulfur species (SO₂, H₂S, S₈⁰) are analyzed by ion chromatography, after conversion to SO₄, which allows the detection limit to be lowered significantly with respect to the previous studies; (iii) appropriate aliquots from intermediate steps may be used to determine other species commonly present in volcanic gases such as CO₂, HCl, HF, HBr, HI, and so forth; (iv) determination of all the other gas species is not jeopardized by the proposed method, i.e., one single vial can be used for analyzing the full chemical composition of a volcanic gas with the exception of NH₃. Statistical parameters calculated from gas sampling data at the F5 crater fumarole in Vulcano Island (Aeolian Islands, southern Italy), suggest that the standard error of mean (s/\sqrt{n}) is higher for S (0.10), followed by SO₂, H₂S, and CO₂ (0.04, 0.038, and 0.028, respectively). SO₂ shows the higher variation coefficient (12.1%) followed by H₂S, S, and CO₂ (5.7, 1.5, and 0.8%, respectively). Furthermore, if the time dependence of sampling is taken into account, the measured values, instead of fluctuating in a random manner, tend to follow systematic patterns, out of statistical control, possibly suggesting a sort of natural fluctuation of the volcanic system. Other crater fumaroles from volcanic systems located in different geodynamical areas (Hawaii, USA, El Chichon, Mexico, Poas, Costa Rica) have been analyzed as well.

Volcanoes that experienced recent or historical eruptive activity are generally characterized by a solfataric or fumarolic state. Volcanic fumaroles are usually located in the central part of the main crater and may release gases, in either a diffuse way or localized vents. The chemical composition of crater gases is extremely important in terms of both fluid circulation studies and volcanic surveillance since they may provide useful information

on the status of a certain volcanic system.^{1–9} Generally speaking, volcanic gases mainly consist of H₂O, CO₂, HCl, HF, and sulfur species (SO₂, H₂S, S₈⁰).⁷ Owing to the strong dependence of SO₂ and H₂S on temperature, redox conditions, interaction with surficial aquifers, etc., these species, even at low concentrations, are considered suitable chemical parameters for triggering volcanic eruptions, especially when related, for example, to H₂O, CO₂, CO, and H₂ contents.

However, despite of their importance, few studies are addressed to sampling and analytical methods for determining SO₂, H₂S, and S₈⁰ in volcanic gases.^{6–12} Moreover, these analytical procedures are not suitable when low concentrations of sulfur species are encountered. This study presents a different approach to analyzing the sulfur species in crater fumaroles by using ion chromatography, which allows achieving low detection limits and sensitivity checks, although it is not the amount of sulfur species that is important, but the variation in time of the single species or their ratios with other chemical parameters.^{9,13} To our best knowledge, previous studies carried out by ion chromatography and applied to fumarolic gases were limited to the determination of total sulfur.¹⁴

The method proposed allows detection when very low concentrations (0.01 mg/L as SO₄²⁻, see below) are present. Despite natural fluctuations, in a single fumarolic vent of a certain volcanic system, relatively long sampling time (> 30 min) may reduce error, due to sudden or periodic increase of the concentration of some component, giving an average in time composition.

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An additional method to determine S_8^0 is also presented, this component being a natural complement to SO_2 and H_2S . Its determination can add important information about volcanic systems on both the presence and possible interaction of the uprising gas phases with surficial aquifers and the time necessary for the volcanic fluid to reach the fumarole orifice.

Sampling Procedure and Reactant Synthesis. Gas emissions were collected after the insertion of a titanium tube into the fumaroles or steaming ground. Whatever the gas manifestation, a Dewar quartz or glass tube was attached to the titanium tube to prevent or, at least, minimize condensation. The Dewar end was then connected to preweighted (precision at 0.01 g) and preevacuated 50-mL thorion-tapped tubes¹⁰ to which 20-mL solutions of 0.15 M $Cd(OH)_2$ and 4 M NaOH were previously added. During fumarole sampling, S_8^0 does not react with the alkaline solution while H_2S reacts with Cd^{2+} to form CdS as insoluble precipitate and SO_2 turns into SO_3^{2-} and SO_4^{2-} .

Slow sampling, to avoid air contamination and let acid gases be absorbed by the alkaline solution, is highly recommended, especially when low flux gas emissions are to be sampled. As already pointed,^{10,12} reactions between H_2S and SO_2 during sampling do not significantly occur since CdS precipitation proceeds relatively fast, avoiding reaction of oxi-reduction processes in solution among the sulfur species. Slow bubbling and gentle mixing during sampling in order to obtain a homogeneous sampling is preferable although it may take a long time before the NaOH solution is saturated. Besides, high-temperature fumarole discharges may cause the NaOH solution to boil, so that the pressure of the solution may get higher than that of the fumarole itself and the alkaline solution may be sucked back into the gas vent. This can partly be minimized by wrapping the vial with wet tissues to maintain the alkaline solution below the boiling point. For this reason, sometimes it is preferred to take a shorter, fixed, sampling time (30–40 min), especially if we also consider that most of the crater fumaroles are located in unhealthy and hazardous areas.

Reference standards of SO_2 , H_2S , and S_8^0 to test the accuracy and precision of an analytical method are not available. Thus, to evaluate the precision and possible natural fluctuation of the system, a new sampling geometry for collecting volcanic gases has been adopted and is shown in Figure 1. This was applied to the F5 crater fumarole (La Fossa Crater, Volcano, Aeolian Islands, southern Italy). This fumarole has a typical composition of volcanic gases with an outlet temperature of 573 K. A Dewar quartz tube with four sampling inlets was connected to the titanium tube. This allows simultaneous collection of four gas samples at predefined times (~30 min). Before inserting the new sample batch, we waited for 15 min. This procedure was repeated four times, thus representing a relatively continuous sampling of ~160 min. The analytical data are summarized in Table 1.

Reagents. As $Cd(OH)_2$ is not usually available from chemical firms, we synthesized it from $CdCO_3$, which is highly toxic. Its preparation is rather delicate even because $CdCO_3$ produces strong exothermic reaction. A slightly excess (~0.2%) of $HClO_4$ (70% w/w) is gently dropped onto powdered $CdCO_3$ by using ultrahigh-quality (UHQ) water. This allows dissolution of the precipitate and eliminates CO_2 . Then, with an excess (~2%) of leached NaOH pellets, precipitation of $Cd(OH)_2$, suitable for

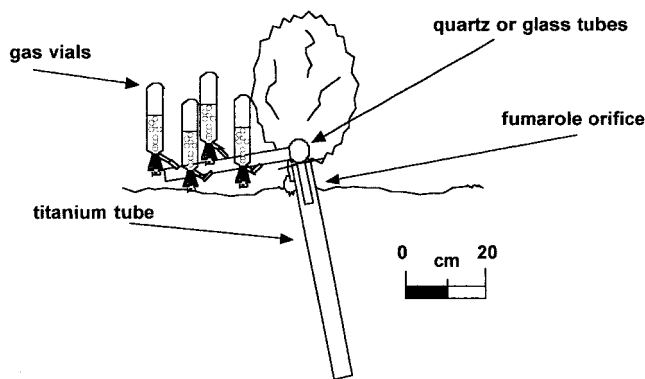


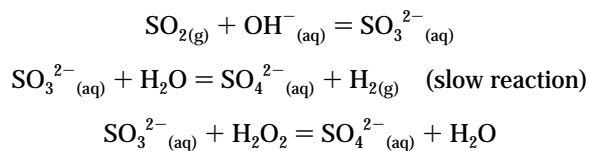
Figure 1. Schematic representation of crater fumarole sampling collection consisting of a titanium tube with Dewar quartz or glass tubes at which the sampling vial is connected. In the present study, the gas sampling geometry has been modified in order to collect simultaneously four gas samples.

purification via centrifugation, is obtained and, finally, rinsed with UHQ water and 2 g/L NaOH. Pure $Cd(OH)_2$ is added to a 4 N NaOH solution to obtain a 0.15 M $Cd(OH)_2$ suspension, and then the resultant mixture is boiled to degas the reactant.

Separation of the Sulfur Species. After sampling, the gas vial consists of the following components: (i) headspace—residual gas fraction (N_2 , He, CO, O_2 , Ar, and other noble gases, H_2 , CH_4 , and other organic gases); (ii) solution—condensed water steam and neutralized acid gases, e.g. HCl, HF, HBr, H_3BO_3 , HI, NO_x , CO_2 , SO_2 , and SO_x ; (iii) solid phase—unreacted $Cd(OH)_2$, CdS (derived from H_2S and H_2S_x that reacted with $Cd(OH)_2$), and other particles carried in by the volcanic gas.

After weighting the vials, gas chromatographic analyses of the gas residual fraction were performed by Shimadzu 14 and 15A chromatographs using He or Ar carriers and TCD or FID detectors according to the different gas species determined. The solution and the solid phase were transferred to PTFE tubes by a siphon connected to a water pump and centrifuged at 15 000 rpm and 290 K for 15 min. Temperature was controlled to prevent the heating induced by high rotation speed. After the supernatant was transferred to a 100-mL flask, as an analytical caution, precipitates were rinsed with UHQ water and once again centrifuged. The second supernatant was then transferred to the same flask where the first aliquot was stored. The solution obtained was then made to 100 mL. An aliquot of 20 mL was used to analyze CO_2 (as HCO_3^-) by automatic titration with HCl and HF (as F^-) by potentiometry while another aliquot of 20 mL was used to analyze HCl (as Cl^-) by ion chromatography.

Determination of SO_2 . To 50 mL of the previous solution, 5 mL of H_2O_2 (30% w/w) was added to oxidize all the sulfur species to SO_4^{2-} , which is the most thermodynamically stable species although not the only one in solution, and this is due to the naturally slow kinetics of reactions:



Then, all SO_x species can be determined as SO_4^{2-} and analytically referred to SO_2 . The solution is buffered by adding

Table 1. Concentrations of SO₂, H₂S, S₈⁰, HCl, and H₂O for Repeated Gas Sampling at Fumarole F5 at Vulcano Island (Aeolian Islands, Southern Italy) and Selected Fumaroles from El Chichon (Mexico), Kilauea (Hawaii, USA), and Poas (Costa Rica)

| gas sample | locality | concentration, % w/w | | | | | |
|--------------------|----------------------|----------------------|-----------------|------------------|-----------|-----------------|------------------|
| | | HCl | SO ₂ | H ₂ S | S | CO ₂ | H ₂ O |
| fumarole F5 | vulcano, Italy | 0.056 01 | 0.436 72 | 1.083 38 | 0.000 247 | 12.87 | 85.55 |
| | | 0.059 66 | 0.402 88 | 1.027 52 | 0.000 218 | 14.68 | 83.83 |
| | | 0.056 77 | 0.402 95 | 1.094 78 | 0.000 045 | 13.20 | 85.24 |
| | | 0.061 79 | 0.461 35 | 1.168 08 | 0.000 257 | 11.35 | 86.96 |
| | | 0.193 54 | 0.341 50 | 0.993 06 | 0.001 516 | 17.96 | 80.51 |
| | | 0.175 35 | 0.343 93 | 0.995 24 | 0.001 556 | 17.06 | 81.42 |
| | | 0.178 64 | 0.348 15 | 0.965 91 | 0.001 508 | 19.63 | 78.87 |
| | | 0.203 10 | 0.344 03 | 0.972 87 | 0.001 728 | 22.80 | 75.68 |
| | | 0.119 06 | 0.450 29 | 1.242 69 | 0.000 819 | 18.00 | 80.18 |
| | | 0.118 18 | 0.467 82 | 1.261 97 | 0.000 713 | 30.34 | 67.81 |
| | | 0.107 72 | 0.450 48 | 1.214 29 | 0.000 813 | 21.45 | 76.77 |
| | | 0.111 84 | 0.437 43 | 1.216 28 | 0.000 813 | 22.49 | 75.75 |
| | | 0.109 35 | 0.448 15 | 1.398 40 | 0.000 503 | 19.18 | 78.86 |
| | | 0.106 14 | 0.465 23 | 1.399 53 | 0.000 487 | 26.47 | 71.56 |
| | | 0.102 82 | 0.465 12 | 1.398 63 | 0.000 469 | 21.10 | 76.93 |
| | | 0.109 25 | 0.477 43 | 1.425 89 | 0.000 521 | 25.07 | 72.92 |
| Big Pool fumarole | El Chichon, Mexico | <0.000 01 | 0.000 20 | 0.174 20 | 0.000 870 | 3.00 | 96.82 |
| Down Pool fumarole | El Chichon, Mexico | <0.000 01 | 0.000 60 | 0.463 80 | 0.033 333 | 6.46 | 93.04 |
| Fumarole F1b | El Chichon, Mexico | <0.000 01 | <0.000 05 | 0.211 80 | 0.002 090 | 5.51 | 94.28 |
| C1 fumarole | Kilauea, Hawaii, USA | <0.000 01 | 13.333 33 | 0.120 40 | 0.006 670 | 3.55 | 82.99 |
| C2 fumarole | Kilauea, Hawaii, USA | <0.000 01 | 15.833 33 | 0.150 50 | 0.010 170 | 3.61 | 80.39 |
| Pared Sur fumarole | Poas, Costa Rica | 0.049 00 | 11.130 00 | 0.270 00 | 0.064 000 | 1.68 | 86.81 |
| Domo fumarole | Poas, Costa Rica | 0.287 00 | 1.040 00 | 0.161 00 | 0.002 900 | 0.18 | 98.33 |

~0.05 g of H₃BO₃ prior to the analysis. Buffering at pH 9.2 is carried out, although it is important that H₃BO₃ ensures the complete neutralization of NaOH due to the pH sensitivity of the ion chromatographic columns.

Determination of H₂S. The solid residue from the centrifugation is successively oxidized by adding 5 mL of H₂O₂ and 0.25 g of NaOH (~1 pellet) dissolved in 10 mL of UHQ water. This allows the dissolution of CdS, converting sulfide to sulfate, the latter being soluble in this medium. Periodic stirring ensures the total dissolution of CdS. H₂O₂ is added in two steps to avoid vigorous bubbling of O₂, with possible loss of the oxidizing efficiency. Overnight rest usually allows the complete release of O₂. Two-step centrifugation is carried out as described for SO₂. The final solution is made up to 100 mL and is suitable for analyzing H₂S as SO₄²⁻ by ion chromatography after buffering with boric acid at pH ~9.2, as previously described.

Determination of S₈⁰. The solid residue mostly consists of Cd(OH)₂, S₈⁰, and small impurities dragged up during the gas sampling. To solubilize S₈⁰, an apolar medium such as CCl₄ is used. After the addition of 5 mL of CCl₄, a few drops of HCl (37%) are gently poured to dissolve the excess of Cd(OH)₂. Complete dissolution of Cd(OH)₂ and S₈⁰ in CCl₄ is favored by stirring the solution for a couple of minutes. One hour is generally needed to obtain the gravimetric separation of two immiscible phases: (i) H₂O with CdCl₂, HCl, and some impurities and (ii) CCl₄ with S₈⁰. The CCl₄ solution is transferred to a 50-mL flask to which 20 mL of UHQ water was previously added. Thus, phase-transfer oxidation may be carried out in two phases. The first one consists of adding 0.5 g of KBrO₃, 0.5 g of KOH, and 0.02 g of KI. The I⁻ ion oxidizes to I₂, which dissolves in CCl₄. S₈⁰ oxidation takes place and the polar compound S₂I₂ forms. The latter is removed from CCl₄ and passes to the first immiscible phase. Here, S₂I₂ oxidizes to SO₄²⁻ and I₂ by KBrO₃. The newly formed I₂ dissolves in CCl₄

and so on. The I₂ in excess turns CCl₄ to purple, suggesting that the oxidative process gets to an end. Eventually, H₃BO₃ is added as previously described. S₈⁰ is then determined as SO₄²⁻ by ion chromatography.

Chromatographic Considerations. Chromatographic analyses are performed with a Dionex DX100 ion chromatograph, equipped with an Ionpack AS14 column. A 1.9 mmol/L Na₂CO₃ + 0.8 mmol/L NaHCO₃ solution was used as eluent. Under such analytical conditions, SO₄²⁻ has a retention time of ~13.5 min. and well separates from both SO₃²⁻ (retention time, 12.3 min) and iodate (retention time, 16 min) (Figure 2). SO₃²⁻ is an intermediate product of sulfur species oxidation processes. Owing to the slow kinetics of such reaction, it is often necessary to add 5 mL of 30% H₂O₂ in the dilute samples before injection into the ion chromatograph in order to complete SO₃²⁻ oxidation. The presence of both SiO₃²⁻ (deriving from SiO₂ basic hydrolysis) and HCOO⁻ (due to CO hydrolysis¹⁵), whose peaks are characterized by retention time of 1.4 and 2.7 min, respectively (Figure 2), does not allow F⁻ determination by ion chromatography. For this reason, a classical potentiometric method may be preferred. On the contrary, Cl⁻ determination does not overlap with any other component (Figure 2). All the aliquots for each of the gas species (SO₂, H₂S, S₈⁰, CO₂, HCl) were analyzed three times.

Buildup of Gas Composition. Gas analytical data are generally referred to as percent by volume or by weight. Gas chromatographic analyses of incondensable gases are calculated as percent by volume, while those of sulfur species are in percent by weight. To build up the gas composition for these species, we have to determine CO₂ by potentiometric titration and then, with the sample weight ($\Delta w = W_{as} - W_{bs}$, where W_{as} is the weight of the vial after sampling and W_{bs} is the weight of the vial before sampling), we may calculate the weight percentage of CO₂ and that of the sulfur species:

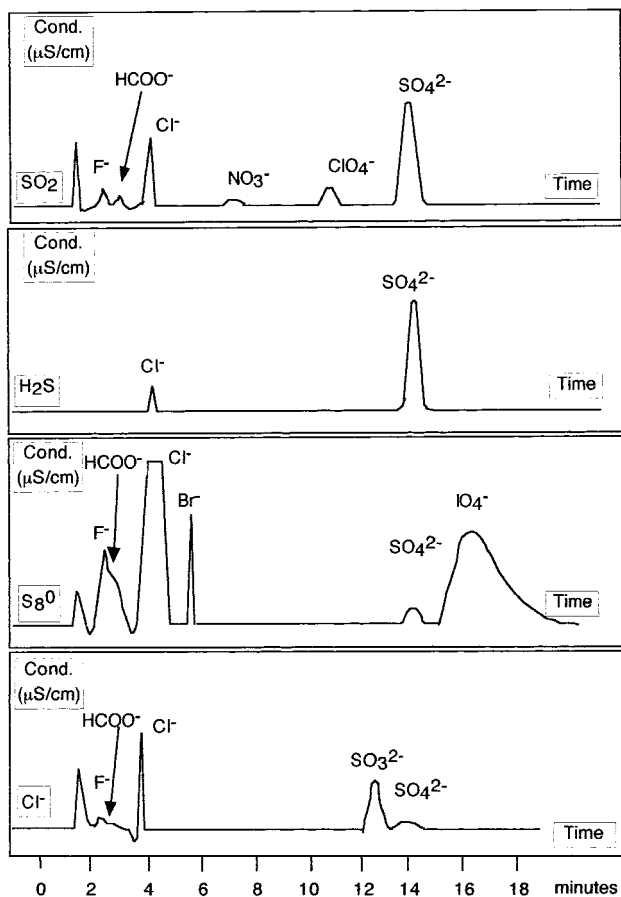


Figure 2. Chromatograms for SO_2 , H_2S , and S_8^0 , after conversion to SO_4^{2-} and Cl^- .

$$\text{SO}_2 \% \text{ by wt} = \text{SO}_4^{2-} (\text{FW SO}_2 / \text{FW SO}_4^{2-}) (0.11 \text{ L}) \times 100 / (1000 \times \text{sample wt in grams})$$

Volume of 0.11 L derives from the addition of 5 mL of H_2O_2 to an aliquot of 50 mL.

$$\text{H}_2\text{S} \% \text{ by wt} = \text{SO}_4^{2-} (\text{FW H}_2\text{S} / \text{FW SO}_4^{2-}) (0.1 \text{ L}) \times 100 / (1000 \times \text{sample wt in grams})$$

$$\text{S}_8^0 \% \text{ by wt} = \text{SO}_4^{2-} (\text{FW S} / \text{FW SO}_4^{2-}) (0.02 \text{ L}) \times 100 / (1000 \times \text{sample wt in grams})$$

$$\text{CO}_2 \% \text{ by wt} = (\text{HCO}_3^- \text{ titrated mol/L}) (\text{FW CO}_2) (0.1 \text{ L}) \times 100 / (1000 \times \text{sample wt in grams})$$

$$\begin{aligned} \text{H}_2\text{O} \% \text{ by wt} = & [(\text{sample wt in grams}) - \\ & (\text{CO}_2 \text{ wt in grams}) - (\text{SO}_2 \text{ wt in grams}) - \\ & (\text{H}_2\text{S} \text{ wt in grams}) - (\text{S}_8^0 \text{ wt in grams})] \times \\ & 100 / (\text{sample wt in grams}) \end{aligned}$$

It must be taken into account that any other gas species $>0.01\%$ in weight, i.e., above the experimental weighting error, needs to be subtracted from the latter formula.

Eventually, percentages by volume of all the gas species can be calculated by theoretical gas equations, e.g. van der Waals.

RESULTS AND DISCUSSION

Statistical Significance of the Analytical Data. Many statistical methods are available to verify the homogeneity of a set of

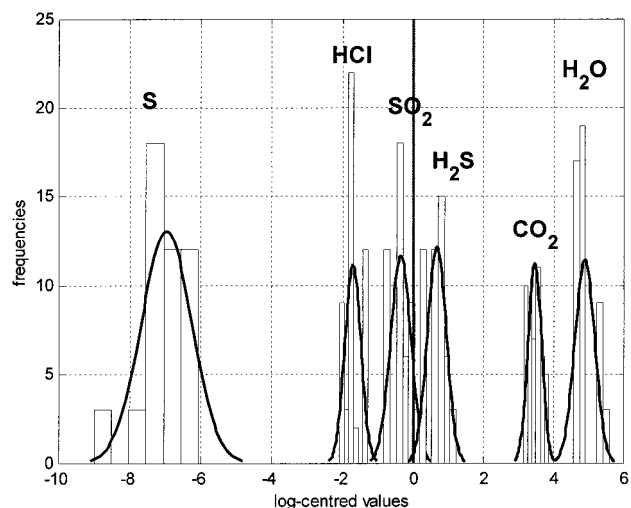


Figure 3. Histograms and normal density curves for log-centered transformed data. The vertical line on zero value represents the sum of variable values for each observation after transformation.

values. Some of them investigate randomness against the alternative of a specific type of nonrandomness whereas others check for a gradual increase or decrease in the values expected if data show marked shift in their relative levels. This situation typically occurs in processes that involve sample batches in which replicate measurements correspond to different sampling times, as in our case. Before studying this aspect in detail, an analysis of the frequency distribution of each measured variable was performed to check representative mean and variance values with the aim of finding an estimate of precision. Since data are compositions, closed to 100, to overcome numerical constraints, the log-centered transformation¹⁶⁻¹⁸ is applied. In fact, in describing data variability, a center, around which the variability takes place, and measures of dispersion around this center, have to be defined for compositional data that are located in a constrained sample space, called simplex S^{D-1} , a subspace of R^D , where D are the composition components. In our case, given the observation

$$S = (x_1, x_2, \dots, x_N) \quad (1)$$

where x_i are the percentages of N variables, the transformation is expressed as

$$S^{\text{tr}} = (\ln[x_1/g], \ln[x_2/g], \dots, \ln[x_N/g]) \quad (2)$$

where g , the geometric mean of observation S , can be calculated as

$$g_s = (x_1 \cdot x_2 \cdot \dots \cdot x_N)^{(1/N)} \quad (3)$$

as a consequence, the raw percentage data are replaced by the logarithms of the ratios between these percentages and the geometric mean. After application of this centered log-ratio

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Table 2. Descriptive Statistics for Log-Centered Transformed Variables^a

| | lc-HCl | lc-SO ₂ | lc-H ₂ S | lc-S | lc-CO ₂ | lc-H ₂ O |
|--|---------|--------------------|---------------------|---------|--------------------|---------------------|
| mean | -1.7065 | -0.3480 | 0.6783 | -6.9739 | 3.4637 | 4.8863 |
| median | -1.7553 | -0.3339 | 0.7276 | -6.9981 | 3.4720 | 4.7622 |
| std dev | 0.2265 | 0.2905 | 0.2677 | 0.7122 | 0.1915 | 0.2829 |
| minimum | -2.0793 | -0.8239 | 0.2046 | -8.9977 | 3.1694 | 4.5629 |
| maximum | -1.2882 | 0.2339 | 1.2246 | -6.0929 | 3.8418 | 5.5763 |
| range | 0.7910 | 1.0579 | 1.0199 | 2.9048 | 0.6724 | 1.0134 |
| std error of mean (std dev/ \sqrt{n}) | 0.03269 | 0.04193 | 0.03865 | 0.1028 | 0.02765 | 0.04082 |
| coeff of variation of the mean, % | 1.92 | 12.05 | 5.70 | 1.47 | 0.80 | 0.84 |
| median dev from median, % | 6.7 | 17 | 13 | 42 | 17 | 7.5 |

^a Number of observations for each group was 48.Table 3. Results of Kolmogorov–Smirnov Test To Check Normality of Log-Centered Transformed Variables^a

| normal parameters ^{b-d} | lc-HCl | lc-SO ₂ | lc-H ₂ S | lc-S | lc-CO ₂ | lc-H ₂ O |
|----------------------------------|---------|--------------------|---------------------|---------|--------------------|---------------------|
| mean | -1.7065 | -0.3480 | 0.6783 | -6.9739 | 3.4637 | 4.8863 |
| std dev | 0.2265 | 0.2905 | 0.2677 | 0.7122 | 0.1915 | 0.2828 |
| most extreme differences | | | | | | |
| absolute | 0.208 | 0.145 | 0.147 | 0.133 | 0.101 | 0.278 |
| positive | 0.208 | 0.138 | 0.136 | 0.108 | 0.097 | 0.278 |
| negative | -0.149 | -0.145 | -0.147 | -0.133 | -0.101 | -0.155 |
| Kolmogorov–Smirnov <i>Z</i> | 1.445 | 1.004 | 1.018 | 0.919 | 0.702 | 1.923 |
| asympt sig (2-tailed) | 0.031 | 0.266 | 0.252 | 0.367 | 0.707 | 0.001 |

^a Number of observations was 48. ^b If significance is higher than 0.05 null hypothesis, *H*₀ on normality is accepted ^c Test distribution is normal. ^d Parameters calculated from sample data.

transformation, the variables in each observation sum to zero and classical statistical analysis can be applied.

Histograms and normal density curves, obtained with mean and variance of sample log-centered data, are reported in Figure 3 whereas the results of descriptive statistics and Kolmogorov–Smirnov test for normality are shown in Tables 2 and 3, respectively. Setting aside HCl and H₂O, showing significance lower than 0.05, all the remaining variables can be described by using normal distribution with sample mean and variance. In this case, standard deviation of the log-centered values can be used to estimate precision. However, if the interest is focused on the measuring technique by which the data are obtained, to compare it with an alternative technique, standard deviation that characterizes the statistical population underlying the measurements is a logical criterion to express precision. On the other hand, if the aim is to indicate the reliability of the best value derived from this set of data, as for example the mean, the interest will focus on the uncertainty of this value and the appropriate measure is the standard error of the average. If the standard error of the mean is expressed as a fraction of the measured value, the coefficient of variation of the mean is obtained, a measure derived entirely from the internal variability of the set of data. The standard error is higher for S (0.11), followed by SO₂, H₂S, and CO₂ (0.04, 0.038, and 0.028, respectively) while SO₂ shows the higher variation coefficient (12.1%) followed by H₂S, S, and CO₂ (5.7, 1.5, and 0.8%, respectively) (Table 3). Different parameters, as for example median and median absolute deviation from median, have to be used for H₂O and HCl. The latter variables tend to deviate from normality (positive skewness) possibly because of small condensation films in the Dewar geometry of gas sampling (Figure 1) where HCl may more easily be dissolved. These condensation films are not likely aspirated randomly into the vial, possibly producing the variations observed for H₂O and Cl.

As previously stated, the gas sampling apparatus (Figure 1) where the statistical approach has been carried out is characterized by a particular geometry; i.e., four gas samples can be simultaneously collected. As a consequence, all the previous statistical considerations can be regarded as valid if differences for samples located in external and internal positions (the null hypothesis *H*₀), for each sampling time, are negligible. In our case, the hypothesis has been tested by applying the parametric *t*-test and accepted with a confidence level of 0.01, except for H₂O and HCl. Since this result may be attributable to a nonnormal behavior shown by these two variables in subgroups of samples, pertain to internal and external positions, and analyzed by the application of the Kolmogorov–Smirnov test, an alternative nonparametric test was applied. However, even if a substitute for the *t*-test that does not require a normality assumption, called Mann–Whitney test, was applied, the same conclusions were reached.¹⁹

Stationary in mean and variance of a time-dependent measuring process has been checked by means control charts.²⁰ To construct a control chart for monitoring the mean value, the observations (subgroups of repeated measurements) have to be plotted following their order time. A solid centerline, corresponding to the sample mean \bar{x}_m , as well as dashed lines for the control limits at $\bar{x}_m - 3s$ and $\bar{x}_m + 3s$, called lower (LCL) and upper (UCL) control limits (*s* is the standard deviation), has to be added. The upper and lower control limits help to identify unusually low or high observations discriminating between typical and large variations to be attributable to special causes. For normal distribution when the process is under statistical control, the probability of exceeding such limits by chance is 0.0026. In our situation (graph not

(19) Carlson, W. L.; Thorne, B. *Applied statistical methods*; Prentice Hall: Englewood Cliffs, NJ, 1997.(20) Shewhart, W. A. *Economic control of quality of manufactured product*; Van Nostrand: New York, 1931.

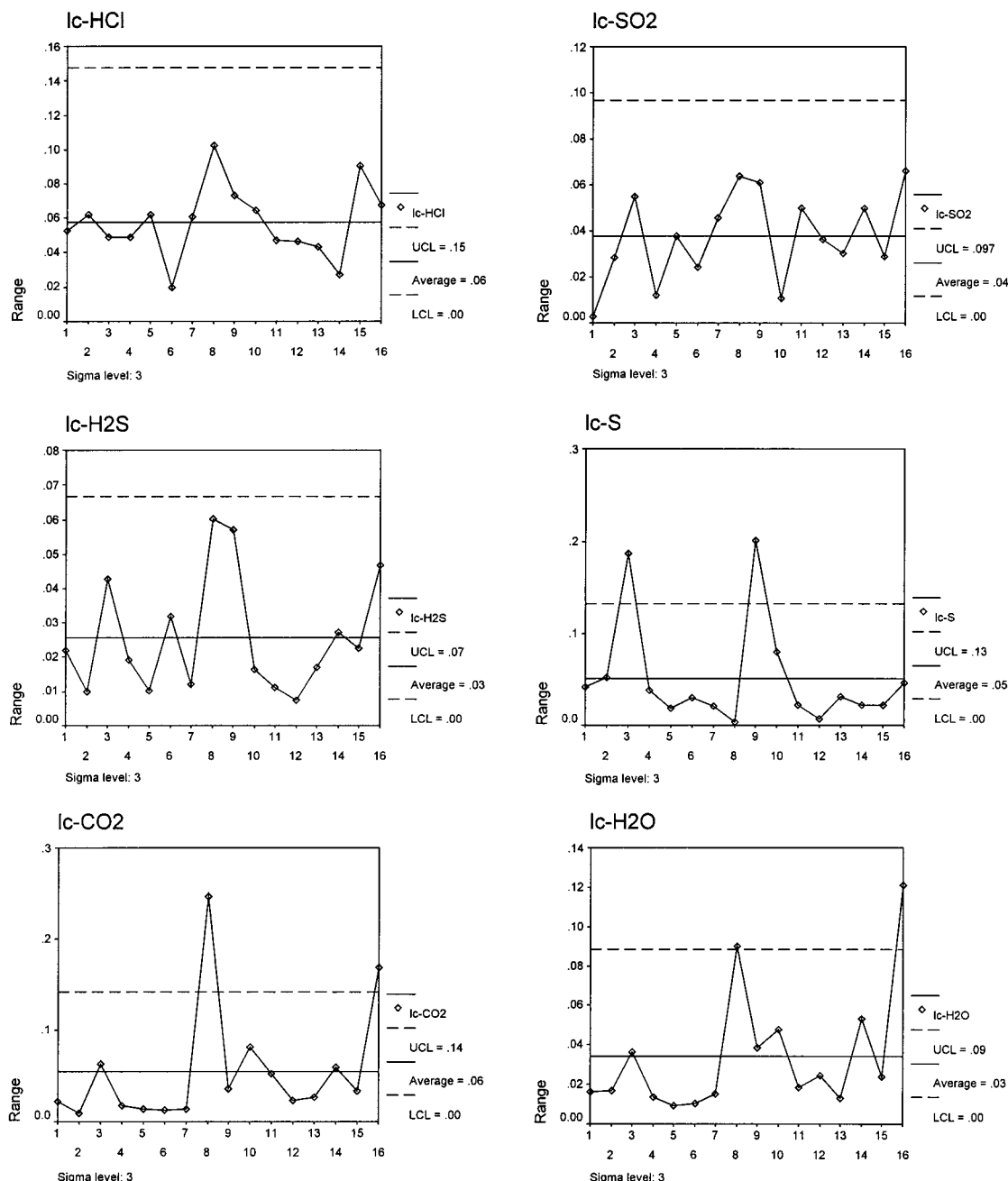


Figure 4. Range control chart for log-centered values.

reported), this monitoring process allowed us to verify that the values, when time dependence is taken into account, instead of fluctuating in a random manner, tend to follow systematic patterns, out of statistical control, suggesting cycling effect (high, low, high) or trend presence.

Another type of control chart, used together with the previous one, investigates the behavior of the range defined as the difference between the largest and the smallest of a set of observations. In a set of values generated by a random process, the ranges of subgroups form themselves into a population. Statistical theory allows estimating the standard deviation of this population using only the average of the ranges and choosing probability limits as for the mean chart.

The average value of the ranges of all subgroups provides a measure for the within-subgroup variability and allows verification

if the average of each subgroup varies by a larger amount. The results for ranges are reported in Figure 4 where statistical control for most of the data is reported (except for a few outlier values for S, CO₂, and H₂O). No systematic changes (nonrandom) are present in the process variability, compared with the result obtained from the x_m control chart.

CONCLUDING REMARKS

Sulfur species in volcanic systems are extremely important for understanding the equilibrium/disequilibrium state of a given system, and thus, the analytical data have to be reliable even when the species are present at very low concentrations. Furthermore, gas sampling and analysis should be carried out in an easy and fast way since it is quite usual to face hazardous and unhealthy conditions. The extremely changeable climatic conditions and the

high altitudes where crater fumaroles are quite often located require easy-to-use and reliable fumarolic gas sampling for sulfur and other critical gas species, such as H_2 , HCl , HF , and CO .

The proposed analytical procedure partly fills this gap with a new analytical procedure that allows determination of SO_2 , H_2S , and S_8^0 in volcanic gases. Moreover, in the sampling vial, incondensable gases and other species commonly present in the volcanic environment, such as CO_2 , HCl , HF , and HBr , can easily be analyzed by gas chromatography, titration, and ion chromatography, respectively.

The statistical approach has evidenced the presence of a trend during the time-dependent gas sampling collection that may suggest a sort of natural fluctuation of the volcanic system. However, this hypothesis needs to be better constrained and investigated in a deeper detail.

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