A Simple Method for the Collection and Analysis of Volcanic Gas Samples

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Abstract

Investigations into the chemistry of volcanic gases depend on the availability of complete and accurate analyses of volcanic exhalations. The wide variety of sampling and analysis methods hitherto used, often supplying only partial analyses of low precision, made intercomparison, and thus a systematic study of volcanic gases, difficult. With the method proposed here, complete volcanic gas samples are obtained permitting the accurate determination of all major species by standard analytical methods without the need for highly specialised ancillary equipment. The samples are collected in evacuated 300 ml pyrex flasks through titanium tubes deeply inserted into the gas vent. Two types of flask are used, a single compartment flask allowing the easy determination of the major constituents and containing 50 ml 4 N NaOH, and a double compartment flask for the separate analysis of the sulfur species and containing 25 ml 0.1 N As_2O_3 in 1 N $HClO_4$ in the first, and 50 ml 4 N NaOH in the second compartment. Non-absorbed gases are determined by gas chromatography, the rest by standard analytical procedures. The determination of H_2O, CO_2, SO_3, SO_2, S_2, H_2S, HCl, HF, H_2, N_2, O_2, CH_4, CO and NH_3 is described.

Introduction

In recent years the processes and mechanisms influencing the chemical composition of volcanic exhalations have received considerable attention. Equilibrium calculations have shown that thermodynamic considerations are useful in explaining many aspects of the observed chemistry of volcanic gases, especially those associated with redox equilibria involving carbon and sulfur species (Ellis, 1957, Heald *et al.*, 1963, Matsuo, 1962). These theoretical investigations, however, are only rarely supported by complete and reliable analytical data. In spite of the vast progress in analytical techniques, the high standard set more than fifty years ago by workers on gases of the Hawaiian volcanoes (JAGGAR, 1940) has only occasionally been reached since. The wide variety of collection and analytical methods nsed (FINLAYSON, 1970; TONANI, 1971), each encumbered to varying degrees with its peculiar faults and deficiencies, renders intercomparison of analytical results extremely difficult, *e.g.* any attempt of a classification of volcanic gases in a manner corresponding to that of volcanic rocks and likely to provide information on their origin or possible differentiation processes, requires large amounts of chemical and physical data preferably obtained and reported by use of uniform and standardised methods.

Many of the methods proposed and in use, though useful in the long term surveillance and possibly the prediction of volcanic activity, can only be applied to the determination of a limited number of species, are too cumbersome or require the use of sophisticated ancillary equipment, *e.g.*, mass spectrometers or highly modified, specially adapted gas chromatographs. The geographically widely scattered and sporadic occurrence of suitable volcanic events and the relatively small number of samples obtained at any time suggest that the method generally applicable should require only a minimum of specialised equipment beyond that available in the average analytical laboratory, with the time needed for carrying out the analyses being only of secondary importance. On the other hand the sampling apparatus itself should withstand, and be usable under, the wide variety of conditions encountered in volcanic gas sampling.

In the following section a short review of available volcanic gas analyses is given to indicate the nature of species and the range of their concentrations likely to be found in the volcanic gas phase and with which the sampling method should be capable to cope.

The Composition of the Volcanic Gas Phase

A preliminary survey of volcanic gas analyses shows that, with very few exceptions, the predominating constituents making up more than 95 % of the volcanic gas discharge, are water vapor and species containing carbon and sulfur in their various oxidation states such as CO_2, CO, SO_2, S_2 and H_2S together with H_2. The relationship between the four elements O, H, C and S involved in the formation of these species is illustrated in Fig. 1 A where the sum of atoms of carbon and sulfur is plotted against the total concentrations of atoms of oxygen and hydrogen reported for volcanic gases from twelve volcanic regions spread all over the world. It is evident that initially all these discharges can be considered to be mixtures of water vapor with carbon dioxide and sulfur dioxide, with the combined effects of the other reduced species being responsible for only very minor deviations from the H_2O-CO_2, SO_2 mixing line. This observation, of course, is in agreement with thermodynamic considerations, which showed that for the temperatures, pressures and oxygen partial pressures prevailing in the magmatic environment, hydrogen, oxygen, carbon and sulfur combine to form predominantly the above three species.

Variations in the proportion of water vapour present are likely to be due to, at least in part, mixing in of non-magmatic water of more shallow meteoric origin. Because of this uncertainty in the origin of fumarolic water, magmatic or meteoric, hydrogen and oxygen are unlikely to provide very useful parameters for the classification of volcanic gases. The origin of carbon and sulfur too is still somewhat obscure, but can be expected to be largely magmatic; because of differences in their chemical behaviour they may provide information on possible differentiation processes affecting the magmatic gas phase. In Fig. 1 B the relationship between water content and total amounts of carbon and sulfur species respectively is shown for the same set of analyses as used in Fig. 1 A and given in Table 1. Values for several individual volcanoes fall close to lines originating from the H_2O corner indicating mixing of water with a gas-phase of a relatively constant C/S ratio. Preliminary checks show that the values for C/S are close to log-normally distributed around the logarithmic mean of $\mu = 0.44$ with a standard deviation σ of 0.53. The analytical data available thus suggest an average ratio C/S in a volcanic discharge of 2.75. The standard deviation given above was obtained by inclusion of all the analyses used in the figures, considering only analyses with water contents below 90 %, σ is reduced to 0.30, with $\mu = 0.40$ remaining virtually the same.

The only other major species not containing the four major elements are hydrogen chloride and hydrogen fluoride. Their concentrations are likely to be controlled by a reaction as symbolized by

$$2\,X^- + H_2O + SiO_2 \rightleftharpoons 2\,HX + SiO_3^{2-}$$

Their presence to any appreciable degree in volcanic discharges thus might be expected to be restricted to areas of andesitic or more acid volcanism where high SiO_2 activities (NICHOLLS, 1971) can be expected for the underlying magma. Low values of S/Cl, however, are observed particularly on island volcanoes, independent of the acidity of the lavas, suggesting that sea-water NaCl may an important role in the production of volcanic HCl. A lognormal distribution similar to that for C/S was found for the ratio S/Cl of analyses providing analytical values for HCl, with $\mu = 1.14$ and $\sigma = 0.58$.

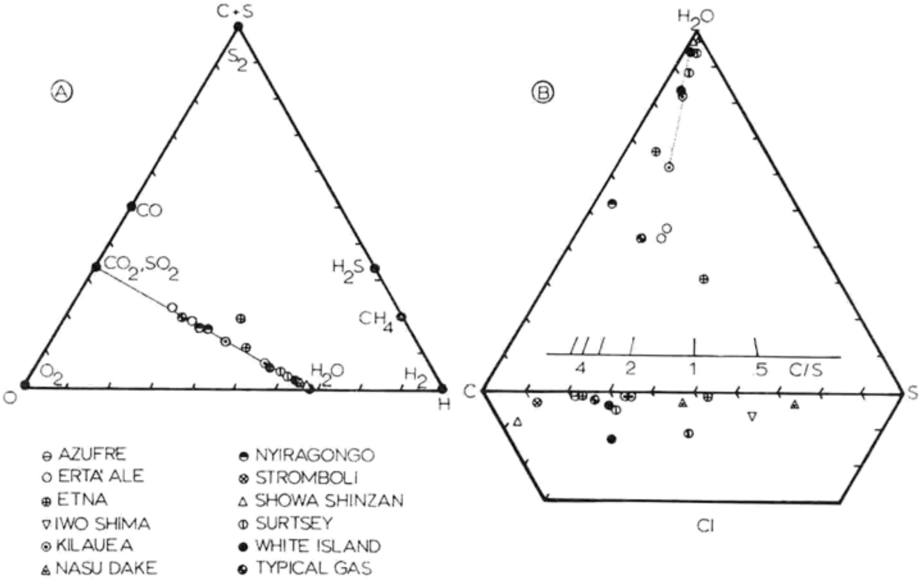

FIG. 1 - Relative proportions of O, H and (C + S), (A), and C, S and H_2O, (B) in gas samples from twelve volcanoes all over the world.

By assuming the lowest water contents observed of around 40 mol-% to be representative of a typical magmatic gas, the primary undiluted mixture produced by a degassing magma then is likely to contain about 40 mol % of each water vapor and carbon species, followed by 15 mol % of total sulfur species and around 1 % HCl, corresponding to ratios C : S : Cl of 72 : 26 : 2. Depending on temperature, the rest is likely to be made up largely of hydrogen, with minor amounts of other hydrogen halides, nitrogen and argon. Additional minor species found are NH_3, H_3BO_3, SiO_2, As, Se and other metallic constituents in the form of oxides or halides. The presence of lower hydrocarbons and other organic compounds has also been postulated (STOIBER *et al.*, 1971).

Method and Equipment for Gas Collection

COLLECTION TUBES

One of the major problems in volcanic gas sampling originates from the use of unsuitable materials for the collection pipes used to conduct the hot and corrosive gases to the sample container. On Surtsey (SIGVALDASON and ELISON, 1968) and White Island (WILSON, 1959) *e.g.* copper and stainless steel tubes were badly corroded in a very short time. This attack on sampling tubes, besides rendering them useless, is likely to lead to serious interference with the chemistry of the volcanic gas stream, *e.g.* partial removal of HCl or H_2S as metal chlorides and sulfides and introduction of heavy metal impurities into the samples accompanied by the production of hydrogen. This latter effect might be responsible for the exceptionally high hydrogen concentrations observed in recent gas analyses from Mt Etna (HUNTINGDON, 1973). In this case some unspecified metal was used. Other materials used for sampling tubes include pyrex and silica glass whose low melting point or mechanical strength limit their use to low temperature or mild emissions of gas.

During work on White Island fumaroles, tubes were tested that showed both high chemical and mechanical stability under fumarolic sampling conditions with temperatures up to 700° C and gases containing up to 2 mol-% HCl and 0.02 mol-% HF. These tubes, made from pure titanium, ca. 2 m long with outside diameter of 2.5 cm at a wall thickness of 1 mm, were left in a fumarolic vent providing the above conditions for several hours without showing any sign of corrosive attack. The high melting point (1675°), mechanical strength, resistance to chemical attack and relatively low price, render pure titanium a material for collection tubes suitable under any likely fumarolic conditions.

The titanium tubes were provided with short, right angle bends ca. 10 cm from one end. By joining two such tubes in varying ways by means of plug-in connections or butyl rubber sleeves, the tube geometry is made somewhat flexible so as to allow convenient connection of the sample bottles for any fumarolic outlet configuration encountered. The transition to the sample bottle was achieved by use of a pyrex reduction piece, again joined to tube and bottle with butyl rubber sleeves (Fig. 2).

SAMPLING FLASKS

Depending on the information desired, one of two types of sample flasks are used. Both allow the determination of the major constituents, with the simpler version being completely adequate for routine analyses. It consists of an evacuated 300 ml cylindrical, round-bottomed flask equipped with a Rotaflo teflon stopcock and containing 50 ml of 4 N NaOH. The tap-like stopcocks used here are superior to any other type as their performance is least affected by the aggres-

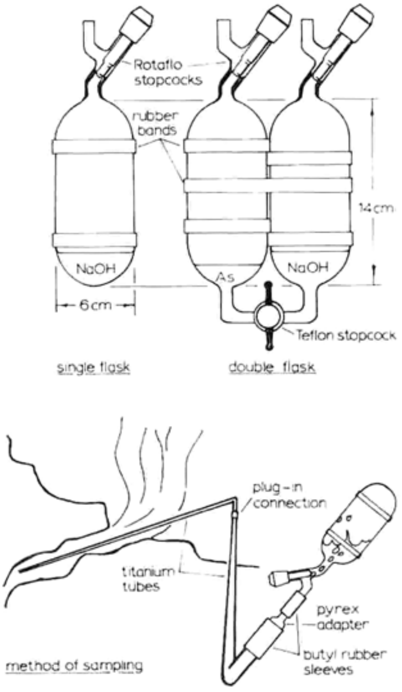

FIG. 2 - Gas sampling flasks and method of gas collection.

sive solutions coming into contact with them and the large variations in temperature during sampling and storage.

The second version consists of two flasks as described above joined on the bottom by a two-way teflon stopcock. One compartment contains 25 ml of a 0.1 N As_2O_3 solution in 1 N $HClO_4$, the other the usual 50 ml of 4 N NaOH. Both compartments are evacuated. In the field the existence of a good vacuum in both types of flask is readily checked by tilting the flask: a characteristic clicking noise indicates that the total pressure in the flasks is very close to the vapor pressure of the solutions inside. A few rubber bands are wound around the upper and lower part of the flasks for protection and more than a dozen of the flasks can easily be carried in a padded box.

SAMPLING PROCEDURE

The absorbing solutions (4 N NaOH, 0.1 N As_2O_3) are fed into the partly evacuated flasks by use of an attached dropping funnel in the laboratory. After evacuating the flasks, « boiling » of the solutions indicates that the vacuum is sufficient, they are weighed to the nearest 1/10 of a gram. By prewarming the flasks and their contents, aspirators can be used for evacuation.

In the field the titanium tubes, joined in a suitable way, are deeply inserted into the fumarolic vent. After flushing the tubes for a sufficient time to remove air the sample flasks are connected. The fumarolic gas is admitted by slowly opening the stopcock. By placing the stopcock lowest, the gases pass through the absorption solutions allowing a high gas flow to be maintained, ca. 30 g of total condensate are usually collected within 5 to 10 minutes. The flow rate then slows down due to warming up of the flask contents, with their vapor pressure approaching atmospheric pressure. By shaking and cooling the flask, however, considerably more condensate may be collected, the final amount obtainable depending on the concentration of non-absorbable gases such as H_2, N_2, CH_4, CO and Ar in the discharge.

Care should be taken that all condensate, sometimes forming in the cooler parts of the collection tubes when low temperature fumaroles are sampled, is transferred to the sample flask. This is achieved by placing the flask as low as possible, so as to allow condensate to accumulate in the pyrex adapter where it is easily detected. No T-pieces should be used between collection tubes and flask as they may lead to preferential loss of some of the constituents and enrichment in others.

The overall procedure for collection with the double flasks is similar. The collection tubes are connected to the arsenic-containing compartment, again the flask is tilted so as to allow the gases to pass through the absorbent, after pressure equalization largely due to accumulation of unabsorbed CO_2, the connecting stopcock is opened carefully, gentle shaking causes the acid gases to be rapidly absorbed by the alkaline solution in the second compartment; the gas flow can be regulated by use of the connecting stopcock so as to avoid splashing over of arsenic solution. After completion of sampling all stopcocks are securely closed.

ANALYSIS OF COLLECTED GASES

After returning to the laboratory the sample flasks are weighed again to determine the total amount of condensate collected. Several methods then may be used to determine the non-absorbed gases, largely H_2, CH_4, CO, N_2 and possibly O_2. During the present investigations these gases were analysed by gas-chromatography after separation on a 5 m long column of molecular sieve 5 Å at room temperature with Argon at a flow rate of 15 ml/min as carrier gas and a thermal conductivity detector. The sensitivity for all gases, except H_2, can be increased by use of He as carrier gas. The total pressure in the sample flasks at room temperature was usually around 50 mm Hg.

After analysis of non-absorbed gases is completed, the condensate solution is drawn from the inverted sampling flask into a partly evacuated aspirator bottle. The alkaline samples together with blanks of the 4 N NaOH absorbent then are diluted to 200 ml with deoxygenated, distilled water, and analysed for CO_2, total sulfur, HCl, HF and the average oxidation state of sulfur.

A) Alkaline Iodine Titration of Reduced Sulfur Species: 2 ml (or a multiple) of alkaline condensate (made up to 200 ml) are added to 5 ml 4 N NaOH (2.5 times the amount of condensate). After dropwise addition of sufficient N/10 iodine solution under shaking and gentle warming to create a permanent yellow color, the clear solution is acidified with 20 ml 2N H_2SO_4 (10 times the amount of sample). The

TABLE 1.

	°C	H_2O	CO_2	SO_2	H_2S	HCl	CH_4	CO	H_2	
Ebeko (IVANOV, 1957)	100	—	92.0	3.9	—	—	—	0.6	0.8	*a*
Erta' Ale (TAZIEFF, 1972)	1075	40.4	29.9	18.3	0.18	—	—	1.1	2.3	*b*
	1075	36.8	31.2	18.2	0.04	—	—	1.1	2.8	*b*
Etna (HUNTINGDON, 1973)	1000	23.2	21.3	23.4	4.51	0.15	1.1	2.3	30.3	*c*
	900	58.2	24.1	4.5	1.70	0.15	—	—	5.7	*d*
Galapagos (COLONY, 1973)	150	—	13.0	3.4	0.09	0.06	—	0.1	—	*e*
Iwo Shima (IWASAKI, 1965)	740	98.1	0.3	0.4	0.03	0.05	—	—	0.2	*f*
Kilauea (JAGGAR, 1940)	1000	57.4	22.9	12.7	—	0.12	—	0.7	0.6	*g*
(FINLAYSON, 1968)		79.3	11.6	6.5	—	0.10	0.4	0.4	0.6	*h*
Nasu Dake (KUSAKABE, 1969)	450	99.2	0.2	0.2	0.3	0.02	—	—	0.04	*i*
Nasu Dake (IWASAKI, 1965)	540	98.0	0.5	0.1	0.3	0.03	—	—	0.04	*j*
Nyiragongo (CHAIGNEAU, 1960)	980	42.9	33.3	3.7	—	—	—	2.0	0.4	*k*
	980	—	68.2	6.6	—	—	—	3.2	1.3	*l*
Stomboli (CHAIGNEAU, 1965)	200	—	49.5	6.9	—	2.60	0.4	7.2	31.8	*m*
Showa Shinzan (MIZUTANI, 1962)	725	99.3	0.4	.01	—	0.04	—	—	0.2	*n*
Surtsey (SIGVALDASON, 1968)	1400	82.7	7.6	3.6	—	0.60	—	0.5	4.7	*o*
	1400	87.9	2.7	2.9	—	0.77	—	0.2	2.7	*p*
White Island	550	82.6	11.8	3.8	1.1	0.57	—	—	0.1	*q*
(GIGGENBACH, 1974)	540	93.2	4.1	1.1	0.5	0.91	—	—	0.1	*r*

a, average of two analyses, no value for water reported (vol-%)
b, average of four analyses with low O_2-contents
c, average of 1970 analyses
d, of 1971 analyses
e, average of three semiquantitative analyses, water free
f, average of two analyses
g, average of 6 analyses, designated excellent
h, « Typical Hawaiian Gas »
i, average of two high temperature samples
j, average of two samples
k, average of two samples collected in CaC_2-tubes
l, average of five samples collected in P_2O_5 tubes
m, average of two analyses
n, average of two analyses
o, average of first four low O_2 analyses (5.64-2.65)
p, average of last four low O_2 analyses (9.66-3.67)
q, average of five high temperature fumaroles sampled in Nov. 1971
r, same fumaroles in Feb. 1972. (All analyses, reporting values for H_2O, in mol-%)

excess iodine liberated is back titrated with N/10 thiosulfate using sodium starch glycocollate as indicator. Calculate

$$a = \frac{320.6 \text{ (ml N/10 } I_2)}{\text{(ml sample)}}$$

In strongly alkaline solution iodine disproportionates into iodide and hypoiodite, the latter is capable of oxidizing all possible sulfur species present, HS^-, $S_2O_3^-$, SO_3^{2-} and polythionates to sulfate (NORKUS and SHAMKYAVICHYUTE, 1971). Together with the total amount of sulfur, to be determined gravimetrically, the average oxidation state can be calculated.

B) Oxidation of Sample with H_2O_2: To 50 ml of alkaline sample in a 100 ml volumetric flask 3 ml of 30 % H_2O_2 are carefully added. The sample should be clear and colorless, the presence of heavy metal impurities may cause catalytic decomposition of the peroxide before oxidation of the sulfur species is achieved. After about 10 min. put on water bath to complete reaction and to destroy excess H_2O_2, if necessary add another 3 ml H_2O_2. Let cool fill to 100 ml. The resulting oxidized sample is used for all further analyses.

C) Total Sulfur: Add 10 ml of oxidized sample to 50 ml 1 N HCl, place on water bath, when hot add 10 ml of 10 % $BaCl_2$ solution, let cool over night, determine $BaSO_4$ gravimetrically and calculate the total amount of sulfur collected (in mg):

$$b = 5.5 \text{ (mg } BaSO_4)$$

The average oxidation state of sulfur then is given by

$$\bar{n} = (6b - 2a)/b$$

Assuming the total sulfur discharge to be made up of only SO_2 and H_2S, thus neglecting the presence of elemental sulfur and sulfuric acid, the amount of sulfur dioxide collected is given by

$$\text{(mg } SO_2 \text{ collect.)} = 2\,(4b\text{-}a)/3$$

and that of H_2S

$$\text{(mg } H_2S \text{ collect.)} = 1.06\,(a\text{-}b)/3$$

D) *Hydrogen Chloride*: 10 ml of oxidized sample are added to 30 ml 2 N H_2SO_4 and titrated with N/10 $AgNO_3$ potentiometrically or in neutral solution according to Mohr.

$$(\text{mg HCl collect.}) = 146\ (\text{ml N/10 Ag NO}_3)$$

E) *Carbon Dioxide*: 2 to 10 ml oxidised sample are diluted with 50 ml distilled water. After adjusting, by use of a pH-meter, the pH of the solution first with 2 N HCl, then with N/10 HCl to 8.25, the solution is titrated with N/10 HCl to pH 3.8.

$$(\text{mg CO}_2\ \text{collected}) = 1760\ (\text{ml N/10 HCl})/(\text{ml sample})$$

F) *Hydrogen Fluoride*: Fluoride is determined by use of an Ion-Specific electrode on 5 ml of oxidized sample, ten times diluted with a 0.2 N citrate buffer at pH 6.

G) *Water*: The water content of the fumarolic discharges is taken as the difference between the weight of the total amount of condensate collected and the sum of the amounts of species collected. Only a small error is likely to be introduced by assuming SO_2 and H_2S to represent all the sulfur species sampled.

After conversion of the analytical results to moles collected, the final results are expressed in mol-%. This latter concentration unit appears to be the most convenient and allows rapid and easy intercomparison of results. Mol-% is readily entered in thermodynamic calculations by use of the relationship

P_i = (mol-% P_t/100, where P_i represents the partial pressure of the gas at total pressure P_t.

The above collection technique also allows the determination of SiO_2, NH_3, As, Se and other metallic trace constituents in addition to other minor non-absorbed gases such as lower hydrocarbons and rare gases. For routine surveillance purposes, however, the determination of water (*G*), carbon dioxide (*E*), total sulfur (*C*) and hydrogen chloride (*D*) is sufficient.

A more detailed determination of the actual sulfur species present in the fumarolic discharges is made possible by use of the double flasks. After collection, these flasks, preferably still hot, are placed horizontally with their connecting stopcock open to allow passage of residual acid gases still present in the acid compartment into the alkaline compartment. The alkaline condensate is analysed as above. After extraction of the acid solution, the precipitates of As_2S_3 and elemental sulfur are separated by use of glass filter crucibles. The filtrate made up to 100 ml is analysed for sulfate, chloride and fluoride in a manner corresponding to that for alkaline condensates. The filter crucible containing the solids As_2S_3 and sulfur is placed into a small beaker, and after addition of 2 ml of 30 % H_2O_2, warmed to about 60° C. Only As_2S_3 is oxidized, leaving elemental sulfur unattacked. The crucible is washed, all rinsing solutions are carefully collected and used for precipitation of the sulfide-sulfur fraction as $BaSO_4$ in the usual way.

TABLE 2 - Comparison between analytical results for sulfur obtained by use of the single and double compartment flasks (in weight % elemental sulfur).

Fumarole	*Sampl.*	*Single Flask*		*Double Flask*					
No.	*Date*	*S*	$\bar{n}$	*S(+6)*	*S(+4)*	*S(O)*	*S(−2)*	*S**	$\bar{n}$*
5	9.7.72	1.077	2.48	0.016	0.840	0.094	0.186	1.136	2.62
6	9.7.72	1.352	3.34	0.023	1.182	0.086	0.058	1.361	3.48

* calculated from double flask results

The elemental sulfur remaining on the crucible is oxidized with bromine after addition of water and a drop of CCl_4. The next day the resulting sulfate is precipitated as $BaSO_4$. In total four fractions of $BaSO_4$, suitable for isotopic analysis, are obtained:

1. The fraction entering the flask in the form of SO_3 or sulfuric acid and accumulating in the acid filtrate. Only little sulfur was usually found to be present in this form.

2. That originating from SO_2 and absorbed in the alkaline compartment.

3. Elemental sulfur, whose origin might be due at least in part, to reaction of H_2S and SO_2 in the sampling train. Preliminary isotopic studies, however, strongly suggest it to have been present in the original discharge.

4. The fraction having reacted with As (III) to form As_2S_3 and being present in the discharge as H_2S.

In Table 2 typical analytical results for the sulfur species present in two fumaroles sampled by use of the two types of flasks are given. The agreement between total sulfur contents and average oxidation states determined by the two methods is satisfactory; the assumption, however, that the sulfurous discharge is made up of only SO_2 and H_2S, as used in evaluating the distribution of sulfur species from analyses on single flask samples, is an over-simplification and the values obtained have to be considered to be only approximations.

With the general nature of volcanic gases roughly established, future attempts should be directed towards obtaining accurate and complete analyses of volcanic emanations over extended periods of time from as many sources as possible. The simple method for collection and analysis proposed here might enable such work to be carried out especially in areas where limited instrumental facilities could prevent full exploitation of many opportunities.

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