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A new method for sampling fumarolic gases: Analysis of major, minor and metallic trace elements with ammonia solutions

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Abstract

A new method using ammonia solutions in pre-evacuated quartz bottles has been experimented for volcanic gas sampling and analysing. Various tests (reproducibility, variability and comparison with known methods such as NaOH pre-evacuated bottles and acid condensates) have been performed to check for their efficiency. By using ammonia solutions, acid gases (St, HCl, HF), carbon dioxide, noncondensible gases (N_2, Ar, …) and metallic trace elements (MTE) can be measured with standard methods (HPLC, GC, titrimetry, ICP-MS).

Results show that acid gases, CO_2 and noncondensible gases are sampled and analysed with similar efficiency in NH_4OH bottles than by using the known and accurate NaOH method. Moreover, a key point is that NH_4OH solutions, after undergoing adequate processing (oxidation and acidification) allow also precise MTE measurements by using standard ICP-MS methods. Such MTE measurements appear much more reliable than those performed on acid condensates.

Pre-evacuated ammonia bottles appear therefore as an optimum tool to collect volcanic gases and to obtain their complete chemical composition.

Keywords: volcanic gas; sampling; acid gases; noncondensible gases; metallic trace elements

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1. Introduction

Volcanic gases are complex mixtures of H, C, O, S, minor acid gases (HCl, HF, HBr), trace gases (He, Ne, …) and metallic trace elements (named MTE in this work : Pb, Se, Cd, Bi …). A very reliable method for sampling such mixtures was proposed by Giggenbach (1975). It uses NaOH as a reactant in empty bottles, and is now by far the most widely used method for the detection of all the above-mentioned species except MTE (Giggenbach and Matsuo, 1991; Giggenbach et al., 2001). These last elements are commonly sampled by collecting the so-called "acid condensates", in spite of evident sampling bias such as MTE revolatilisation and scavenging by S precipitation (Bichler and Sortino, 1995b; Toutain et al., 2000). However, the availability of high precision data for MTE concentrations in magmatic fluids is highly needed to constrain the dynamics of gas cooling (Symonds et al., 1987; Quisefit et al., 1988) and elemental flux calculations. Moreover, MTE have been shown to potentially mark fluctuations of magmatic activity (Quisefit et al., 1988; Toutain et al., 1995; Goff et al., 1998; Shevenell and Goff, 2000), making them potential tracers for monitoring

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of volcanic activity. Herein, we propose another simple and accurate method similar to that of Giggenbach (1975) but using NH_4OH reactant in place of NaOH. By using such a method, the complete and quantitative analysis of all species (acid gases, CO_2, noncondensible gases, MTE) is easily performed. In this paper, we will validate the method by 1) establishing the good reproducibility of each measurement on NH_4OH bottles and 2) comparing chemical compositions obtained on NaOH, water condensates and NH_4OH bottles collected simultaneously. We believe that this method is reliable for routine measurements in most observatory conditions as it uses classical and widespread analytical techniques (High Pressure Liquid Chromatography, Gas Chromatography, titrimetry, ICP-MS). Volcanic fluids used for this comparison are from Vulcano (Aeolian Islands, Italy) and Merapi (Java, Indonesia).

2. Previous methods

2.1. Acid condensates: an open system

Measuring MTE in volcanic gases is a constant goal since many years. Different collection systems have been employed to condense the high-temperature gas phase, including direct condensation through a silicon or silica tube (Piccardi, 1982; Gemmel, 1987; Africano, 2004), or forced condensation in a condensor cooled by cold water, snow, ethanol dry-ice or ether (Quisefit et al., 1989; Taran et al., 1995; Goff and McMurtry, 2000). Such methods are "open systems" because some species (CO_2, O_2, N_2, Ar, He, H_2, …) have to be released to the atmosphere. Moreover, as the natural flow available at most high-temperature fumarolic vents is low, it has to be forced by using either manual or electric pumping to allow a significant volume of fluid to be collected. The solution therefore obtained is supposed to contain the water, acid gases (SO_2 as $SO_4^{2-}+SO_3^-$, HCl and HF as Cl^- and F^-) and MTE, which are thought to be dissolved in the solution. Such solutions display usually very low pH values (often close to 0) and are not suitable for S (partial dissolution of sulphur species) and CO_2 measurements. Such acid condensates have 2 main advantages: significant volumes are easily sampled, and their bulk chemistry supplies analytical matrix well adapted to the usual instrumental conditions for MTE analysis.

These solutions, however, have some characteristics that are rarely discussed in the literature, except Fischer et al. (1998):

- a white to pale yellow precipitate often appears within the solution quickly after collection. This is the result of S precipitation, which acts usually with a high kinetic. Recent results on acid condensates from Kudryavy volcano (Fischer et al., 1998) show that such precipitates are potentially MTE-rich (up to 33, 8 and 5 ppm for Pb, Bi and Rh, respectively). S precipitation may also remove trace elements showing high chemical affinity with S, such as Se, Te, As (not analysed in Fischer et al. (1998)), in accord with the chemical composition of solid sulphur deposited around low temperature fumarolic vents (Greenland and Aruscavage, 1986; Toutain, 1987; Quisefit et al., 1989).
- These solid phases remain floating in solution, but are also adsorbed on the inner face of collecting flasks making S-budgets poorly constrained.
- During sampling, the collected solution may remain in the device at relatively high temperature (typically 30–50 °C, depending on gas temperature, input flow and capacity of the device) whereas the atmosphere above the solution is depressed as the result of pumping. This may lead to revolatilization of some MTE, the level of which likely increases with the volatility of the element. Bichler and Sortino (1995b) have shown that appreciable amounts of MTE were detected at the outlet of the condensate collector and concluded to their transport from the solution as volatile species, which are up to now non-identified.

All these factors probably arise in the collection of solutions depleted in the most volatile MTE, which are also those of the highest volcanological interest (As, Se, Te, Tl, Pb, Bi, Hg, Cd, Zn, Sb). Acid condensates therefore display both a very high variability and possibly non-reliable MTE concentrations even if their high absolute content is an advantage for the determination of some MTE present at low amounts in volcanic gases.

2.2. Caustic bottles: a close system

Giggenbach (1975) described a powerful method for sampling volcanic gases by using bottles under vacuum and partially filled with 4N NaOH. This procedure allows the dissolution of most of the compounds (H_2O, CO_2, SO_2, H_2S, HCl, HF, MTE), whereas non-condensable species (H_2, N2, Ar, O_2, He, CO) remain in the gas phase within the bottle. It enables considerable enrichment of the solution in trace species and operates in close system, without any leak to the atmosphere. Soda solutions were recently experimented for MTE analyses in Vulcano and Kudryavy fumarolic fluids (Bichler and Sortino, 1997;

Fischer et al., 1998). They may appear as suitable for this objective, but due to the Na-bearing matrix, high dilution of the solutions (typically 1:250) and specific apparatus (high-sensitivity sector-field ICP-MS or INAA) where needed, that makes this procedure rather difficult for multi-elementary and routine measurements. Moreover, the use of caustic solutions prohibits analysis of Na^+ and K^+ ions in solution, which may be good indicators in hydrothermally derived fumarolic systems. There is therefore a need for a reliable sampling method and simple analytical procedures allowing both MTE and major gases routine precise measurements on a single sample.

Our objective was to setup a complete method allowing both the easy sampling and the routine multi-elementary analysis of major species, minor species and MTE on a single sample. Bichler and Sortino, 1995a, 1996, 1997; Bichler et al., 1999 investigated the potentialities of various solutions such as Tris(hydroxymethyl)aminomethane, NaOH and NH_4OH for trapping and analysing MTE in fumarolic fluids. They concluded by using precise INAA measurements that NH_4OH was the best trapping solution owing to both its high level of purity and its applicability to a large range of elements (Bichler et al., 1999). However, because INAA needs both heavy installations and at least 2 months delay for radioactive decay of Na, it does not appear as a convenient and largely available method for routine analysis. Therefore, we selected ICP-MS for MTE measurements. To establish the reliability of this new method, volcanic gases trapped in NH_4OH solutions are compared for CO_2, acid gases, noncondensible gases and MTE concentrations with samples collected simultaneously by using NaOH bottles or gas condensates.

3. Sampling

3.1. Sampling sites

Merapi (Indonesia) and Vulcano (Italy) were chosen for their easy access to fumarolic fluids with a wide range of outlet temperatures.

— *Merapi* in Central Java is an andesitic, very active dome-forming and explosive volcano. The activity of Merapi is characterised by repeated episodes of dome growth and collapses (Voight et al., 2000). Merapi emits high temperature gases (up to 911 °C in 2000) that can be collected in 2 fumarolic fields, namely Gendol and Woro, the former being systematically hotter than the latter. The chemistry of fumarolic gases was already studied (Le Guern and Bernard, 1982; Symonds et al., 1987; Symonds, 1993).

— *Vulcano* is the southernmost island of a volcanic arc named Aeolian Archipelago in Southern Italy. Its active cone (La Fossa) is 391 m a.s.l., and has erupted for the last time in 1888–1890 (Keller, 1980) with phreatomagmatic to magmatic episodes producing viscous trachytic to rhyolitic pyroclasts. Since this event, and apart constant and low temperature hydrothermal manifestations at sea bottom, the activity is limited to fumarolic manifestations at La Fossa crater with strong temporal fluctuations of flow rates and gas temperatures (maximum temperature of 700 and 475 °C measured in 1993 and 2006, respectively). Water and acid gases (SO_2, H_2S, HCl, HF) are dominated by a magmatic component (Bolognesi and D'Amore, 1993; Chiodini et al., 1993, 1995; Capasso et al., 2001).

3.2. Gas collection

Table 1 displays the different samples together with collection parameters. Gas vents were selected at Merapi and Vulcano on the basis of their outlet temperature in order to cover a large range of temperatures. Quartz "Dewar" tubes 0.7 m long and 1 cm diameter were used for collecting gases. Solid ashes transported by the gas flow were blocked for most of them during sampling by inner prominences distributed along the inner wall of the tube.

3.2.1. NaOH bottles

250 cc Pyrex bottles equipped with a Teflon stopcock are partially filled with 50–70 ml of 4 N NaOH for the second set of samples. They are analysed for condensable and non-condensable species following the classical and reliable method already described (Giggenbach, 1975; Sortino et al., 1991).

3.2.2. NH_4OH bottles

They are made of fused quartz to reduce the level of contamination by impurities commonly contained in Pyrex and the adsorption on the inner walls of bottles and are equipped with a Teflon stopcock. Enrichment of trace elements and the collection of a large amount of gas (typically 100–120 g) is obtained by using pre-evacuated (P: 0.5×10^{-2} atm.), 600 ml quartz bottles filled with 100 ml of 4 N ultra-pure NH_4OH (Merck). To obtain low blank values, quartz flasks were successively washed with 30% ultra-pure HNO_3 and 4 N ultra-pure

Table 1
Collecting conditions of the 3 sets of samples at Vulcano and Merapi. F0 and FA (V1, V2, V3) are fumaroles on the rim of Fossa Crater

Sample			Collected		
Name	Site	Fumarole	Samples	Date	Outlet T (°C)
V1	Vulcano	F0	Cond., NH_4OH, NaOH	22/02/01	358
V2	Vulcano	FA	Cond., NH_4OH, NaOH	23/02/01	363
V3	Vulcano	F0	NH_4OH, NaOH	12/04/02	250
V4	Vulcano	beach	NH_4OH, NaOH	14/08/02	100
M1	Merapi	Gendol	NH_4OH, NaOH	28/09/01	660
M2	Merapi	Woro	Cond., NH_4OH, NaOH	21/09/01	590
M3	Merapi	Woro	NH_4OH, NaOH	21/09/01	497
M4	Merapi	Woro	Cond., NH_4OH, NaOH	21/09/01	407
M5	Merapi	Woro	Cond., NH_4OH	21/09/01	311
M6	Merapi	Woro	Cond., NH_4OH	03/03/02	574
M7	Merapi	Woro	Cond., NH_4OH	03/03/02	456
M8	Merapi	Woro	Cond., NH_4OH	13/06/02	297

V4 sample was collected at Baia di Levante beach. Woro and Gendol are the 2 main fumarolic fields at Merapi.

NH_4OH and therefore filled with 100 cc of NH_4OH. By using 600 ml bottles, that is 2–3 times the volume of NaOH bottles used commonly, we collect typically 50 to 100 g of volcanic gas. The weights of solutions are measured prior and after collecting to determine H_2O contents. Solutions are stored in PP bottles cleaned with double distilled HNO_3. It is noteworthy that fused quartz bottles are much more expensive (about 600 €) than Pyrex ones. However, a limited set of 3–4 quartz bottles allows the reliable sampling of a fumarolic system. Because contamination due to bottle alteration by caustic solutions is expected to be much lower when using fused quartz with respect to Pyrex, quartz bottles may also be used with caustic solutions following the procedure described by Fischer et al. (1998), using high-sensitivity sector-field ICP-MS.

3.2.3. Acid condensates

The third set of samples is made of "acid condensates". They are obtained by using a field Pyrex condensor refrigerated with ether (boiling point: 34 °C). Slow manual pumping allows a continuous flow of gases through the device. Solutions are stored in pre-washed PP bottles.

4. Samples analysis and results

Ultra-pure water is obtained from MilliQ™ (Millipore). HF, H_2O_2 and NaOH are "Suprapur" grade (Merck). Ultrapure HNO_3 is obtained in the laboratory by double subboiling in a quartz apparatus.

For acid condensates, fractions of solutions were filtered on 0.45 μm cellulose acetate filters (Millipore) prior to major element analysis whereas centrifugation in PP tubes, which induces very low MTE blanks was performed before MTE analyses of both acid condensates and NH_4OH samples. MTE were analysed with a Elan 6000 ICP-MS (Perkin–Elmer), HPLC was performed with a DX300 (Dionex) and gas chromatography with a Perkin–Elmer using a double detector (HWD, FID). The analytical procedures are outlined in Table 2.

4.1. Sulfur and halogens

4.1.1. Procedure

Cl^-, F^- and total sulphur as SO_4^- ions are measured by ion chromatography (Sortino et al., 1991). Acid condensates are filtered and analysed following adequate dilution. Both NH_4OH and NaOH trapping solutions follow a different processing due their complex matrix. The exact procedure is displayed in Table 2 and can be generalized as follows:

1) Dilution of the totality of the NaOH and NH_4OH solutions to fixed volumes (usually 250 cc) in ultra-pure H_2O.
2) Oxydation of the diluted NaOH solution (20 cc) or of the bulk NH_4OH solution (20 cc) with 3 cc of 35% ultrapure H_2O_2 for a 30 min duration to oxidize reduced sulphur to sulphate.
3) Warming (20–40 min) of oxidized solutions to remove excess H_20_2 and dilution up to 50 cc with ultra-pure H_2O.
4) Neutralisation of 3 cc of the diluted solutions by ion (H^+) exchange resin (DOWEX 50WX4-50) until pH ~ 7 is reached.
5) Dilution of both solutions (with various dilution factors, depending on the respective concentrations of anions and the calibration ranges chosen).

The reproducibility of the method has been checked by performing 9 replicates (preparation + analysis) on a single sample (V3) and a high level of reproducibility was obtained for Cl^-, SO_4^{2-} and F^- in NH_4OH solutions (Table 3). These results are very similar to statistics performed by Sortino et al. (1991) on NaOH efficiency for acid gases trapping.

Table 2
General description of the respective procedures used for sampling and analysing CO_2 and acid gases

Type of sample	Compounds	Sample processing	Analytical technique	Measured species	Instrumental precision (%)
Acid condensates	HCl, HF	1,3	HPLC	Cl^-, F^-	5
	MTE	2,7	ICP-MS	MTE	1–10
NaOH bottles	St, HCl, HF	3,4,5,6,3	HPLC	SO_4^{2-}, Cl^-, F^-	5
	CO_2	3,4,5	Titrimetry	HCO_3^-	2
	Inc. gases		GC	N_2, CO, Ar …	<5
NH_4OH bottles	St, HCl, HF	3,4,5,6,3	HPLC	SO_4^{2-}, Cl^-, F^-	5
	CO_2	4,8,5	titrimetry	HCO_3^-	2
	Inc. gases		GC	N_2, CO, Ar.…	<5
	MTE	2,4,5,7	ICP-MS	MTE	1–10

1: Filtration of the solution on 0.45 μm cellulose acetate filters (Millipore).
2: Centrifugation of the solution in PP tubes.
3: Dilution with ultra-pure H_2O.
4: Oxydation with 30% ultra-pure Oxygen Peroxyde.
5: Warming of the oxidised solution for elimination of excess H_2O_2 (20–40 min).
6: Neutralisation of the alkaline solution by a ion (H^+) exchange resin (DIOWEX 50WX4-50).
7: Acidification with double distilled HNO_3. 8: 4 N sodium hydroxide addition.

4.1.2. St/Cl ratios

These ratios are key indicators of the origin of gases and of volcanic activity. Comparisons of these ratios measured in NH_4OH, NaOH and acid condensates are displayed on Fig. 1A, B and C). 6 samples allow the comparison of SO_4/Cl ratios (Fig. 1A) between NaOH and NH_4OH samples. All are close to the slope of value 1, except sample M2, which shows a ratio about twice in the caustic bottle with respect to ammonia bottle. This exception has been confirmed by repeated analysis, and is probably due to an artefact during sampling. Except M2 sample, the general good agreement shows that the oxidation of sulphur species to sulphate ions is complete in both solutions and that both the sampling method and the general chemical procedure using ammonia do not fractionate S/Cl ratios.

4.1.3. F/Cl ratios

Numerous samples collected from identical fumaroles during IAVCEI workshops (Giggenbach and Matsuo, 1991; Giggenbach et al., 2001) often display significant fractionation of HCl and HF in samples collected in NaOH bottles. This was interpreted as the result of the high solubility of these compounds that are likely to be fractionated into a liquid phase resulting from possible vapour loss during sampling. Fig. 1B and C does not suggest such effects to occur, with F/Cl ratios being almost similar in soda, ammonia and acid condensates samples. One can remark that F/Cl are more scattered between soda and ammonia bottles, this is probably because these solutions have undergone high dilutions in order to avoid HPLC columns saturation to occur, the precision on the measurement of F contents is therefore seriously lowered with respect to other elements.

4.2. CO_2 determinations

The procedure for NaOH solutions (titration of the basic solution by HCl) is described by Giggenbach (1975). A specific procedure has to be used for NH_4OH bottles to avoid pH decrease during warming of solutions (the pH decrease is due to NH_3 or N_2 loss under warming and leads to CO_2 degassing): 3 cc of bulk NH_4OH are mixed with 0.5 cc H_2O_2 and 1 cc of NaOH to fix a pH of about 13. Solutions are therefore warmed for excess H_2O_2 loss. Both oxidized solutions (NaOH and NH_4OH) are acidified down to pH = 8.1 by using 1 N HCl and therefore down to pH = 4.2 by using 0.1 N HCl. The validity of the method is first established by comparing the repeatability of the sample preparation and CO_2 analysis using both NaOH and NH_4OH flasks (Table 4, upper part). CO_2 concentrations measured in the initial solutions are displayed with mean values together with 1σ standard deviation. As only carbonate species were measured, values are displayed in mg/l of CO_2 instead of μmol/mol. Low and similar relative standard deviation in the ranges 1–2% for both methods evidence that processing ammonia solution does not affect the reliability of the measurement with respect to soda solution. The second step to validate the method is to compare CO_2 concentrations in NaOH and NH_4OH flasks sampled the same day and at the same fumarole. This was

Table 3
Reproducibility for sampling preparation and analysis of acid gases performed on 9 replicates of V3 sample (Vulcano) using the NH_4OH bottle

	Type	n	Cl (mg/l)	F (mg/l)	SO_4 (mg/l)
V3	NH_4OH	9	60,34 ± 1,19	1,80 ± 0,17	193,99 ± 2,41

done for two sets of samples, collected at the Fossa crater and at the beach, each set being constituted by 1 to 9 replicated samples (Table 4, lower part). Results are in good agreement (discrepancy of 6.4 and 9% between soda and ammonia bottles for V3 and V4 sample sets, respectively). This evidences that no CO_2 loss occurs in ammonia solution upon warming due to soda addition, and that carbon speciation in both solution is similar.

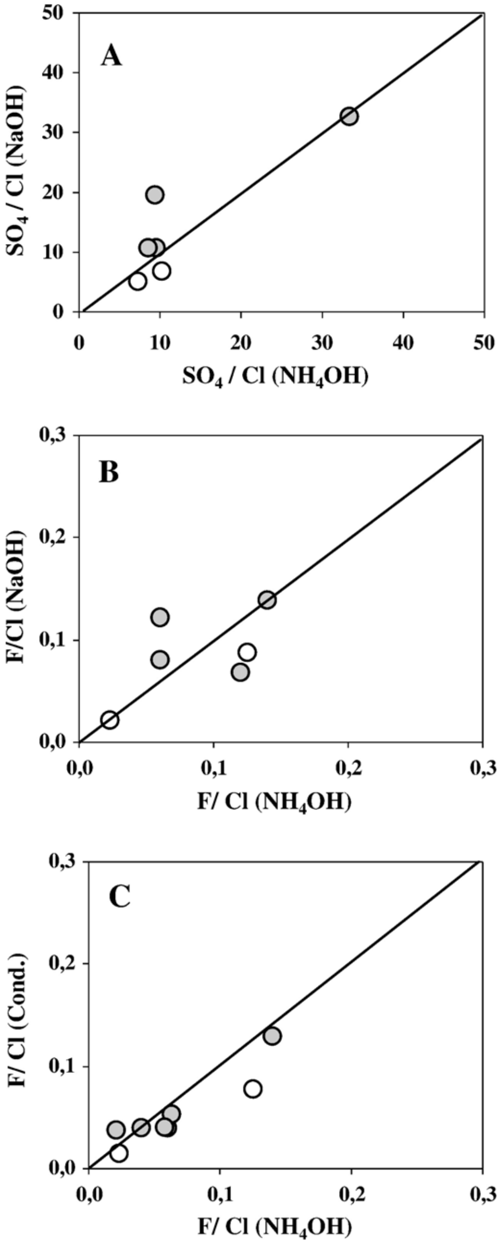

Fig. 1. A: Comparison of SO_4/Cl ratios in NH_4OH and NaOH solutions. B: comparison of F/Cl ratios in NH_4OH and NaOH solutions. C: comparison of F/Cl ratios in NH_4OH and acid condensates solutions. Empty circles are samples from Vulcano. Grey circles are samples from Merapi.

4.3. Non condensible gas

Non condensable species (N_2, Ar, O_2, H_2, CO, He, CH_4) are classically analysed in the gas phase remaining over the solution in NaOH flasks (Giggenbach, 1975; Giggenbach and Matsuo, 1991; Giggenbach et al., 2001). In this work, analyses are performed by gas chromatography (Perkin–Elmer) with a double detector (HWD, FID) with precisions below 5%. The reliability of NH_4OH solution with respect to He, H_2, CO, N_2 and CH_4 has been checked by analysing 8 NH_4OH samples (V3 sample set) collected the same day at the same site (fumarole F0, 12/04/2002). NH_3 which was likely non-measurable over ammonia solutions was not analysed. Analytical results with mean values together with one sigma (1σ) standard deviation are shown on Table 5 in µm/mol of total gas. Standard deviations are in the range 4–12% from CO to CH_4. The highest standard deviation concerns trace species (He and CH_4) and are close to standard deviation measured in soda bottles. The reasonable level of standard deviation calculated for ammonia bottles show that they are suitable for noncondensible gas analyses.

4.4. MTE analysis

As mentioned above, we selected ICP-MS for MTE measurements, for its low detection limit, wide linear dynamic range, multi-element capabilities and high sample throughput, with minor sample preparation, making it usable for routine measurements.

4.4.1. Sample preparation for ICP-MS analysis

Parts of the NH_4OH and gas condensates samples were centrifuged in double distilled HNO_3 pre-washed PP tubes (30 ml). This procedure (Table 2) allows the separation of sulphur precipitates and ashes from the aqueous fraction with low blanks. Due to their extremely low weight fractions, residues were not analysed. Aliquots of NH_4OH samples were treated with 0.5 ml of ultra-pure H_2O_2 to oxidize sulphur species in solution, which might precipitate as solid S during acidification. Samples were then diluted and acidified with double distilled HNO_3 down to total dissolved solids (TDS) <1 g/l. Maximum NH_4OH concentrations obtained in the analysed solutions was 0.3 N whereas HNO_3 concentration was kept constant at 0.6 N. Acid condensates were diluted with double distilled HNO_3 2% down to total dissolved solids (TDS) <1 g/l. An internal standard (In-Re) was added in all analysed solutions to correct for temporal drift. All

Table 4
Upper part of the table: repeatably for sampling preparation and analysis of acid gases performed on *n* replicates of *n* samples in both NaOH and NH_4OH matrix at Vulcano (sample V3) and Merapi (sample M3)

Sample set	Type	T °C	*n*	*n′*	CO_2 (mg/l)	CO_2 (μM/M)
V3	NH_4OH	250	1	9	60,34 ± 1,19	
M3	NaOH	497	1	9	427 ± 5,21	
V3	NH_4OH	250	9	1		48350 ± 1706
V3	NaOH	250	1	1		43999
V4	NH_4OH	100	2	1		64183–63346
V4	NaOH	100	3	1		57371–57928–63797

Lower part of the table: comparison of CO_2 concentrations in NaOH and NH_4OH bottles at 2 different sites at Vulcano (F0 fumarole from Fossa crater and beach fumaroles from Baia di Levante). *n* is the number of samples and *n′* is the number of replicates on a single sample. One standard deviation (1σ) has been calculated for the V3 sample. Absolute values are displayed for other samples.

preparations and analyses were replicated twice. Accuracy and precision of the measurements were controlled by analysing SLRS-4 and SRM 1640 certified reference material. Analytical errors are in the range of 5–10%.

4.4.2. Calibration of NH_4OH matrix

Nitric matrix is usually considered as the most suitable for ICP-MS analysis, because H, N and O are already present in air entrained by the plasma. These elements contribute to the formation of a wide range of polyatomic ions, such as $^{40}Ar^{1}H$, $^{40}Ar^{14}N$, $^{40}Ar^{16}O$, $^{40}Ar^{16}O^{1}H$, the intensity of which is not increased significantly by the addition of an HNO_3 (2%) matrix (Jarvis et al., 1992). However, it was necessary to check the influence of diluted ammoniac matrix because of its higher N, H, O apportion (0.3 N NH_4OH/O.6 N HNO_3) as regard to classical HNO_3 2% matrix. This apportion should not be a major cause of increased polyatomic interferences, but might lead to subsequent changes in the plasma equilibrium (matrix effect). In order to evaluate this effect, a comparison was established by analysing in similar conditions multi-elemental reference solutions, diluted both in 2% HNO_3 and in 0.3 N NH_4OH + 0.6 N HNO_3 matrix. The correlation coefficients (r^2) observed between matrix-matched calibrations curves are in the range 0.99–1 (Fig. 2) for all analysed isotopes. As a similar response is observed for both matrixes, the effect of diluted NH_4OH matrix can be neglected. As a consequence, matrix-matched standards are not required and a single multi-elemental standard (2% HNO_3 matrix) was used for both NH_4OH and acid condensates solutions analysis. This evidences that NH_4OH matrix are suitable for ICP-MS calibration and measurement of numerous MTE.

4.4.3. Interferences due to S and Cl contents

The presence of major elements at high concentrations (Na, S, Cl) in NaOH samples, (S, Cl) in NH_4OH samples and Cl in acid condensates samples might generate spectroscopic or non-spectroscopic interferences during ICP-MS measurements. Various methods such as dilution, precipitation, solvent extraction or online separation are proposed in literature in order to reduce or overcome these effects (Evans and Giglio, 1993; Vanhoe et al., 1994). A well-documented table of polyatomic interferences is also available (May and Wiedmeyer, 1998). In the case of classical volcanic gases measurements, these interferences are not discussed except in Fischer et al. (1998). These authors used a very high dilution (1:250) in order to reduce the interferences during the analyses of NaOH samples by ICP-MS. Such a high dilution was required because of the high Total Dissolved Solids (TDS ≈ 130 g/l) obtained in samples, mainly due to the 5 N NaOH matrix used. A consequence of this dilution is that most of the MTE are undetectable with conventional quadrupole based ICP-MS methods and a high sensitivity, high-resolution instrument has to be used. In the case of NH_4OH samples and acid condensates, the TDS are significantly lower (10 to 20 times) as they are mainly dependent on S and Cl contents in the samples. As a consequence, significantly lower dilutions (1:10 to 1:30) leading to a TDS < 1 g/l during the ICP-

Table 5
Variability ($n = 8$) of non-condensable gas measurements in NH_4OH

	Type	T °C	n	He	H_2	N_2	CO	CH_4
V4A-V12A	NH_4OH	250	8	0.486	47.124	431.183	0.348	0.011
1 sigma				0.042	5.255	39.778	0.041	0.002

Mean and one sigma standard deviation in μm/mol of total gas Analyses by gas chromatography.

MS measurements, are required to minimize the effects of non-spectroscopic interferences during ICP-MS measurements. Therefore, numerous reliable MTE data are accessible without the need of high resolution and sensitivity instruments. However, a particular attention is required for some elements or isotopes, which might be affected by

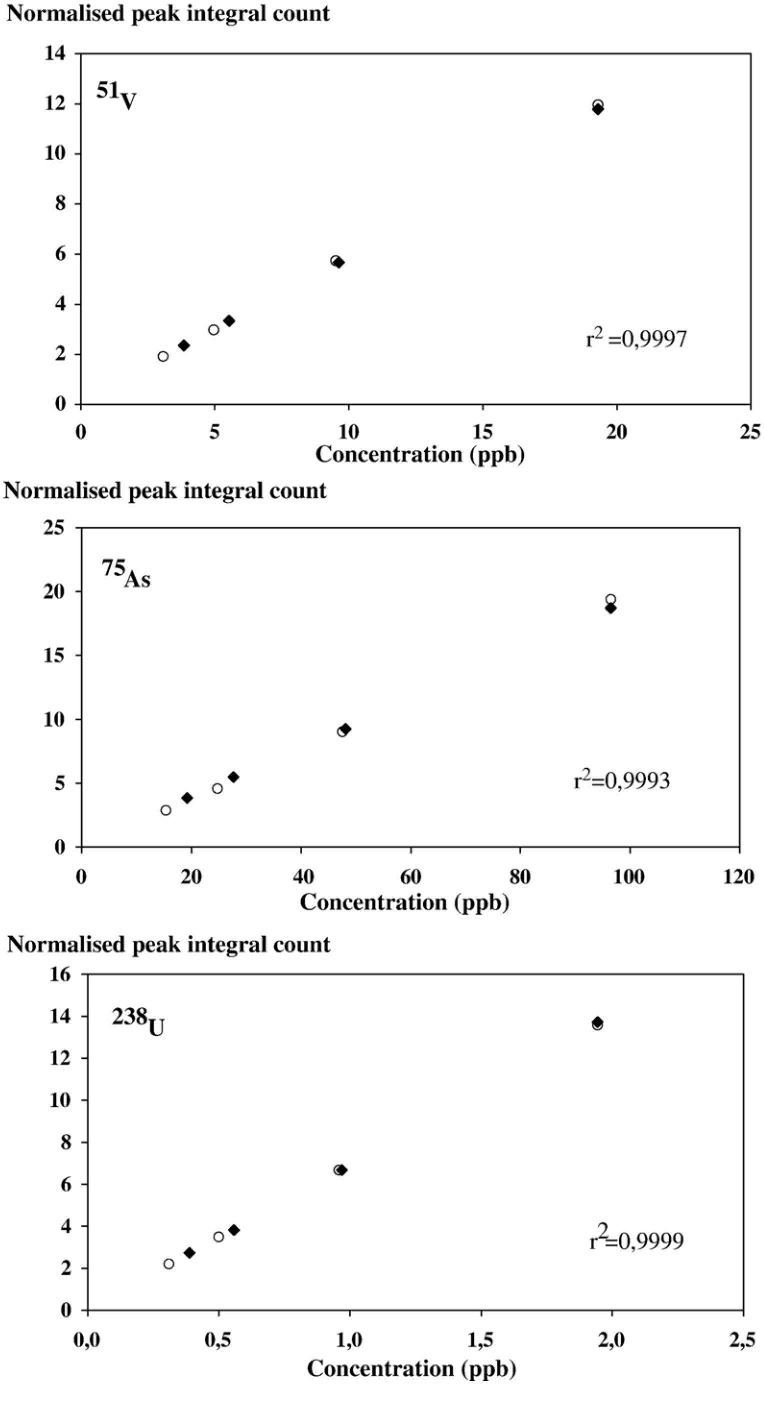

Fig. 2. Examples of calibration curves obtained with multi-elemental reference solution diluted in 2% HNO_3 matrix (empty circle) and 0.3 N NH_4OH/O.6 N HNO_3 matrix (full diamonds) for ^{51}V, ^{75}As and ^{238}U. Rhenium was used as internal standard for peak normalisation. ^{51}V, ^{75}As and ^{238}U where chosen as examples to illustrate the validity of the method across a wide mass range. Correlation coefficients (r^2) observed between matrix-matched calibrations curves are ranging from 0.99 to 1 for all analysed isotopes.

spectroscopic S and Cl interferences even at low concentrations. Following Vanhoe et al. (1994), the main elements concerned are V and As (affected by Cl spectral interferences) and Ti and Zn (affected by S spectral interferences). These interferences might affect both acid condensates and NH_4OH measurements. Acid condensates are more subject to Cl interferences (higher Cl content) whereas NH_4OH samples should be more affected by S interferences (higher S content). In order to check these interferences during our measurements, we used solutions of "Suprapur" grade H_2SO_4 and double distilled HCl, diluted with HNO_3 2% to get a range of standards with concentrations between 50 and 500 ppm for Cl or S. We measured the same isotopes as for the samples, and considered only the isotopes for which we got a linear correlation between interfered isotopes and interfering element (Fig. 3A and B). It was then possible to correct the interferences in the samples, according to their respective S and Cl contents during the measurements. The importance of the interference was calculated directly from the comparison between the apparent analyte concentration (induced from the known S or Cl concentrations in the sample), and the measured concentration. In order to obtain an acceptable precision on the corrected values, results were discarded if the interference was estimated higher than 10% of the total intensity. In many cases, the ratio isotope/interference is high enough, so that the correction is not necessary.

4.4.4. MTE: results

Validating trace elements analysis methods generally needs the use of reference standards analysed together with samples in similar conditions. This procedure can't be applied to volcanic gas samples. The only way to display the efficiency of our method is to compare it with that commonly used by gas geochemists, that is the "water condensate" method and to search for systematic discrepancies that could be interpreted in terms of method respective efficiency. Absolute MTE concentrations

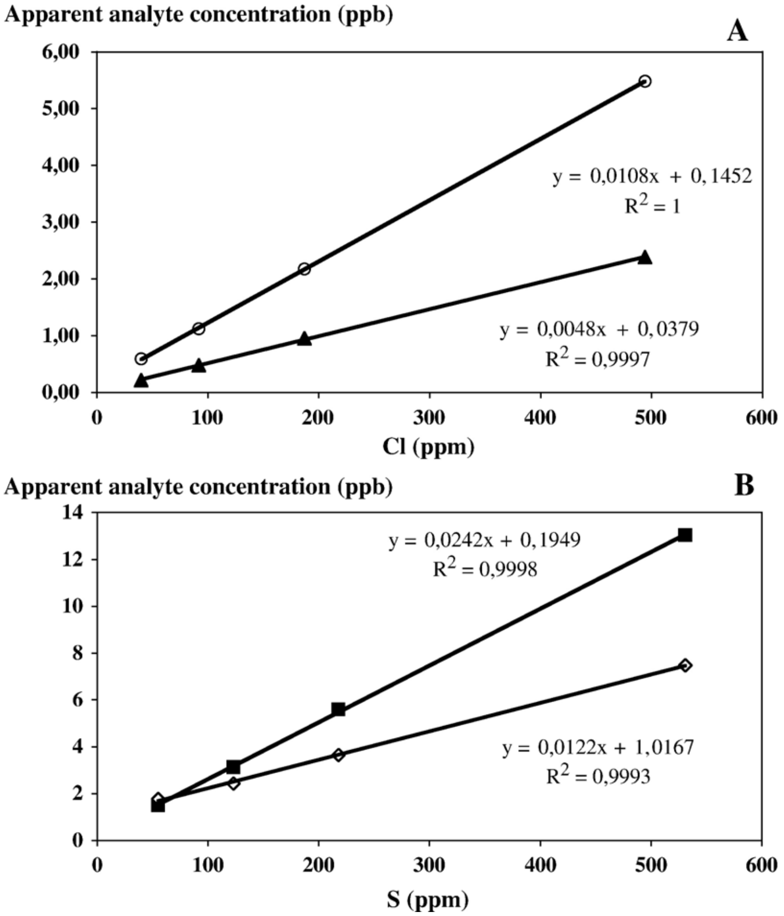

Fig. 3. Examples of linear correlations for Cl (A) and S (B) standards used for interferences calibrations. Apparent analyte concentrations induced by the interfering element are shown for A: ^{51}V (round plot): $^{35}Cl^{16}O$, $^{37}Cl^{14}N$; ^{75}As (triangle plot): $^{40}Ar^{35}Cl$ and B: ^{49}Ti (square plot): $^{32}S^{16}O^{1}H$, $^{33}S^{16}O$; ^{66}Zn (diamond plot): $^{34}S^{16}O^{16}O$, $^{33}S^{16}O^{16}O^{1}H$, $^{32}S^{16}O^{18}O$.

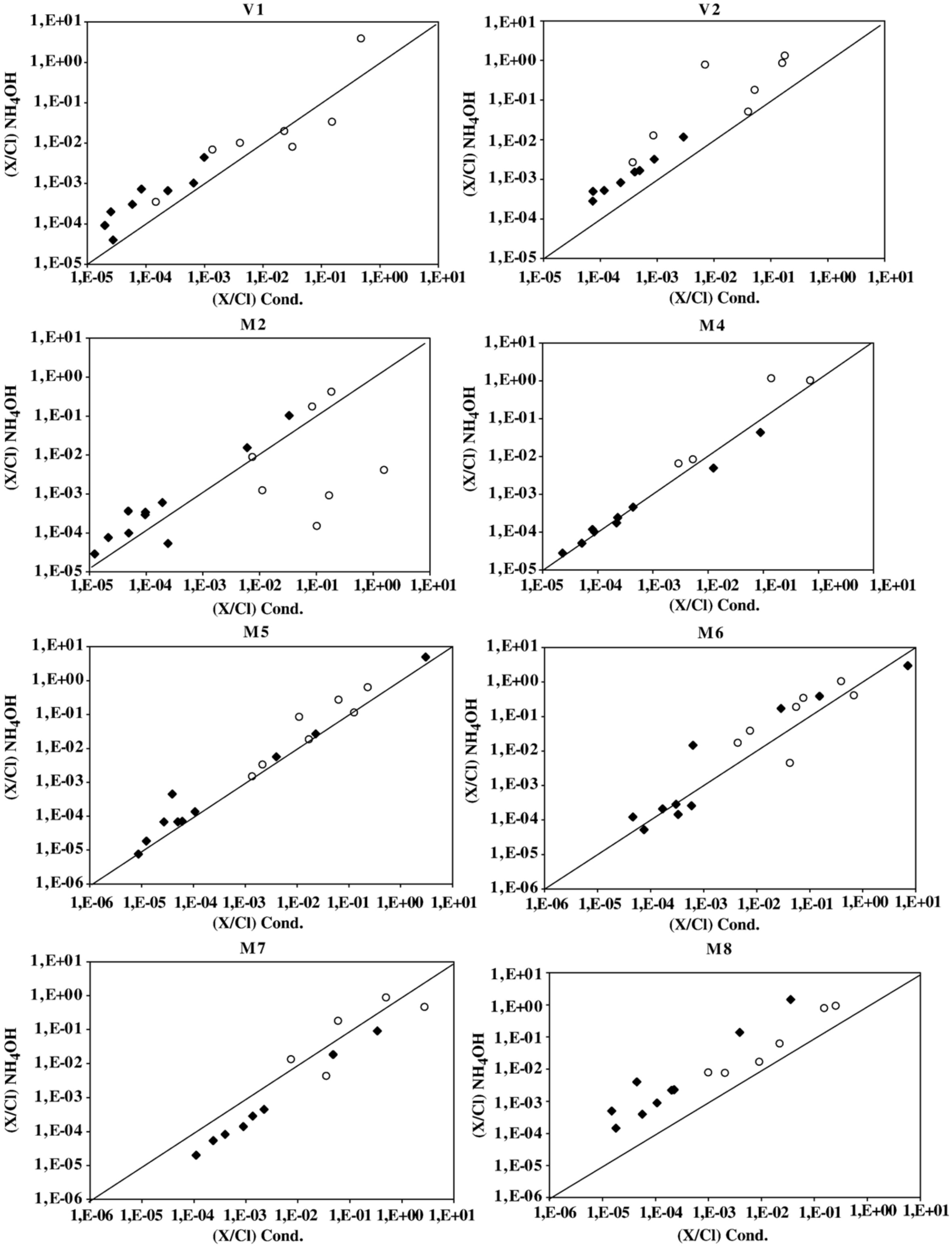

Fig. 4. Comparison of X(ppb)/Cl(ppm) ratios in NH_4OH bottles with respect to the same ratio in acid condensate for volatile elements (empty circles) and refractory elements (full diamond).

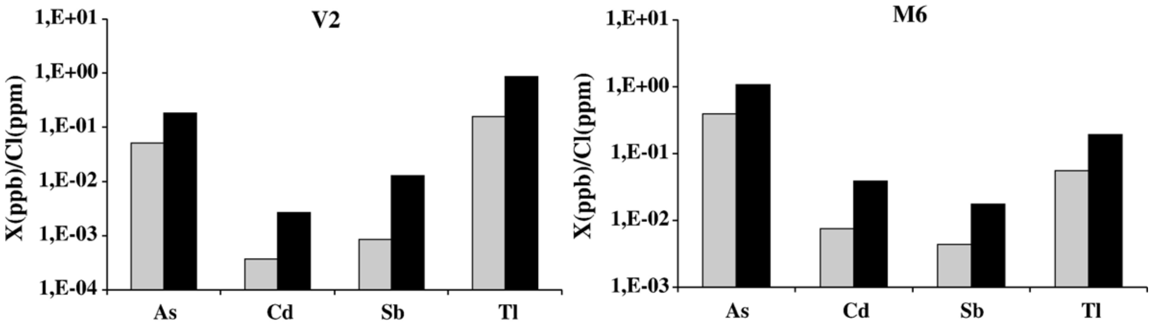

Fig. 5. Comparison of X(ppb)/Cl(ppm) ratios in NH_4OH bottles (black area) with respect to the same ratio in acid condensate (grey area) for some key volatile elements: As, Cd, Sb and Tl. Examples shown for V2 and M6 fumaroles.

cannot be compared in both matrix because 1) the acid condensate does not quantitatively sample gases such as H_2S and CO_2 whereas the ammonia solution does, and 2) dilution by ammonia occurs in NH_4OH bottles. Comparisons of MTE between the 2 methods therefore require to use MTE concentrations normalized to a common element that do not undergo any fractionation during sampling and processing of solutions. Only acid gases can be used for such a purpose. As total sulphur is not trapped in acid condensates and F sometimes displays both some fractionation and shows too low concentrations for accurate measurements, only Cl concentrations are usable. Fig. 4 displays the ratio of each element normalized to chlorine in ammonia with respect to the same ratio in acid condensate for samples V1, V2, M2, M4, M5, M6, M7 and M8. Such plots allow the comparison of the level of enrichment of a given element with respect to chlorine for a same fumarole, in both solutions. Elements are displayed according to their known behaviour in high temperature fumarolic environments: volatile elements are As, Cd, Zn, Sb, Pb, Tl, Bi whereas refractory elements are Mg, Si, Mn, Co, La, Ce, Pr, Nd, Th, U. Even if data are clearly scattered, some features can be outlined. Volatile elements appear quite systematically enriched in ammonia solution compared to acid condensates. Indeed, 50 normalized ratios were obtained for volatile elements and 40 of them indicate a higher or a similar enrichment in NH_4OH solutions with respect to the acid condensate. This enrichment is not T°-controlled and may be related to the fact that acid condensates sampling may lead to revolatilization of MTE or scavenging of elements in solid S, which does not occur by using the closed pre-evacuated ammonia flask. However, 10 normalised ratios indicate that NH_4OH solutions are depleted for some volatile elements (Pb, Bi, Tl, Cd) with respect to the acid condensate. Such depletions arise probably from an inefficient aspiration due to a vacuum problem. Such small aspiration certainly lead to the cooling of volcanic gas before its entrance into the collecting flask and probably allows the formation of liquid phases or solid sublimates potentially Pb, Bi, Tl and Cd rich (Symonds et al., 1987) on the sampling tube walls. The presence of refractory elements in volcanic gases arises mainly from wall rock reactions or particle contaminations (Symonds et al., 1987). Their patterns are mainly dependent of these variable factors but indicate that these elements are adequately trapped by NH_4OH solutions (Fig. 5).

Elements classically used to describe and quantify degassing processes at active volcanoes are the volatile elements. These elements seem to be reliably sampled by using the ammonia bottle, which should avoid possible vapour loss of elements or undesirable scavenging during S precipitation that may occur by using the classical acid condensate method. With sufficient precaution on the vacuum quality within the collecting flask, ammonia bottles appear as the most suitable method to collect and analyse volatile MTE.

5. Conclusion

Ammonia solutions used in pre-evacuated quartz bottles are suitable for volcanic gas sampling and analysing. Various tests (reproducibility and comparison with known methods such as NaOH pre-evacuated bottles and acid condensates) have been performed to check for their efficiency. Standard methods (HPLC, GC, titrimetry, ICP-MS) have been shown to be adapted to analyze acid gases (St, HCl, HF), carbon dioxide, noncondensible gases (He, Ar, …) and MTE in such matrix. CO_2 is analyzed with similar efficiency in NH_4OH and NaOH bottles. This probably results from the same reactions involving CO_2 and both alkaline solutions. As seen from the very similar S/Cl ratios in NH_4OH and NaOH bottles and the good concordance of F/Cl ratios between NH_4OH, NaOH and acid condensates samples, acid gases seem to be correctly analysed by the NH_4OH sampling method. Moreover, noncondensible gases remaining over alkaline solutions are analysed with similar results in NaOH and NH_4OH bottles. A key point is that NH_4OH solutions, after undergoing adequate processing (oxidation, acidification, dilution) allow precise MTE measurements without the need of matrix-matched standards. This shows that NH_4OH solutions are suitable for standard ICP-MS analysis. Volatile MTE concentrations normalized to chlorine are generally depleted in acid condensates with respect to ammonia solutions. This is probably due to revolatilisation and adsorption effects during sampling with the acid condensate technique. However, sufficient precautions on the quality of vacuum in NH_4OH flasks have to be taken in order to avoid undesirable condensation during sampling. These results indicate that MTE measurements performed in NH_4OH solutions appear much more reliable than those performed on acid condensates. Complete chemical composition (major, minor and trace gases) of the gas phase is therefore easily obtained by using pre-evacuated NH_4OH bottles and standard analytical techniques. We believe this new method to be adapted to routine procedures in active volcanology, allowing new approaches on the coupled variability of MTE and major and minor gases in the gas phase.

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