

A COMPARISON OF NEW TECHNIQUES FOR THE DETERMINATION OF MINOR AND TRACE ELEMENTS IN VOLCANIC GASES BY NAA

M. BICHLER, C. PELTZ

*Atominstitut der Österreichischen Universitäten,
Schüttelstraße 115, A-1020 Vienna, Austria
bichler@ati.ac.at*

F. SORTINO

*Istituto di Geochimica dei Fluidi,
Via Ugo La Malfa 153, I-90146K Palermo, Italy*

Minor and trace elements in gaseous effluents from active volcanic areas could be useful indicators for hydrothermal activity. The knowledge of their elemental distribution contributes to a better understanding of degassing processes from various sources. Several methods for the sampling of volcanic gases for NAA are presented and discussed. Absorption by activated charcoal, alkaline solutions like ammonia solution, tetraethylammoniumhydroxide, and tris(hydroxymethyl) aminomethane and ${}^7\text{LiOH}$ solutions were tested in addition to the conventionally applied NaOH solution. The tests were performed mainly at the fumarole fields of La Fossa volcano on the island Vulcano, Southern Italy. Diluted ammonia solution gave the best results.

1 Introduction

Minor and trace elements, transported by magmatic or hydrothermal fluids can be used as indicators for the evolution of volcanic activity, thereby contributing to the complex information necessary for predicting eruptions [1]. The knowledge of trace element distribution is further necessary for a better understanding of volcanic degassing processes. There are three main sources of fluid generation in a volcanic environment: gases, exsolving from the magma (molten rock), the heated host rock and subsurface water reservoirs. Diluting effects by atmospheric or marine waters are known, too [2-4]. Magma degassing occurs at temperatures ranging from about 800° to 1400° due to the pressure release during its ascent through the earth's crust. Depending on the mineral paragenesis of the host rock, the temperature increase causes structural changes like recrystallization, mineral decomposition, loss of crystal water and the simple evaporation of pore water. The temperature gradient leads to ascent and circulation of brines through adjacent porous or shattered rock formations. At elevated temperature and pressure several elements are leached and enriched in the migrating brines. A consequence of decreasing pressure and temperature at some distance from the thermal source is the formation of deposits by precipitation of minerals, often containing sulphides and other ore minerals. The superficial releasing vents of such hydrothermal fluids in volcanic regions are called fumaroles. Their main constituents (H_2O , CO_2 , H_2S , SO_2 , HCl , HF) and a content of incondensable gases like H_2 , N_2 , O_2 , CH_4 and CO can be determined by routine techniques such as titration, HPLC, GC and AAS. The authors' main target was to develop analytical methods for the determination of minor and trace elements [5-10]. This work aims at the evaluation of the techniques applied. The methods comprise sampling of large gas volumes by

filtration and condensate separation as well as the application of various absorption solutions. The objects of investigation were mainly the fumarole fields of La Fossa volcano on the island Vulcano (Southern Italy), but also exhalations at Kilauea (Hawaii, USA) and several thermal springs in Southern Peru.

2 Experimental

Sampling

The main difficulties in collecting volcanic gases for analytical purposes are: avoiding dilution by the ambient atmosphere, excluding contamination by particles and preventing loss of components by condensation due to decreasing gas temperature in the sampling setup before reaching the absorbing agent. These problems were solved using the following procedure: A quartz glass tube of about 400 mm length and 20 mm diameter is inserted nearly completely into the gas releasing vent and connected to a vacuum insulated (Dewar) tube with a spherical joint at the upper end. This is a very simple and effective way to ensure reproducible conditions for the gas sampling itself. However, it must be taken into account that the temperature of the gases to be sampled ranged from 295° to 660° and the escape velocity was sometimes inconveniently high. The average composition of the gases on 21 January 1998 is given in Table 1.

The first technique to collect volcanic gases for NAA was a combination of filtration and condensate separation. The method is described in detail in [7]. Fig. 1 shows the experimental setup with two charcoal filters, a quartzglass cooler and a teflon condensate separator. The gas was pumped through the system by a slow acting teflon membrane pump. The volume of the not absorbed and incondensable gas fraction was measured by a calibrated pump. Being an "open system", this method allows to collect large volumes of gas.

The second technique (Fig. 2) uses a "closed system" as described by Giggenbach [11]. The gases are drawn into an evacuated glass bottle and pass through 50 to 100 mL of an absorption solution. Carbon dioxide, the main incondensable component of the gases and the other acid components should be absorbed immediately and completely by formation of the respective carbonates, sulfates, chlorides etc. Various alkaline absorption solutions were tested and their respective benefits will be discussed. The amount of fumarolic matter collected can be determined easily and accurately by weighing the bottle before and after sampling. In addition to the conventionally applied NaOH solution, dissolved ⁷LiOH and organic absorption media like Tris(hydroxymethyl)aminomethane and Tetraethylammoniumhydroxide were tested. The use of NH₃ in modified quartz glass sampling bottles is the latest method developed and yielded by far the largest number of detectable trace elements.

Table 1. Average composition of volcanic gases, micromol / mol (Vulcano, 21.1.1998, mean temperature 374°C)

H ₂ O	CO ₂	total sulphur	HF	HCl	N ₂	He	H ₂
913000	79460	4894	162	622	903	1.01	264

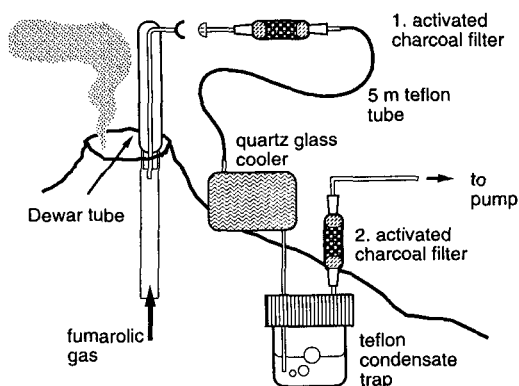


Fig. 1. Sampling setup for volcanic gases by application of activated charcoal and condensate separation

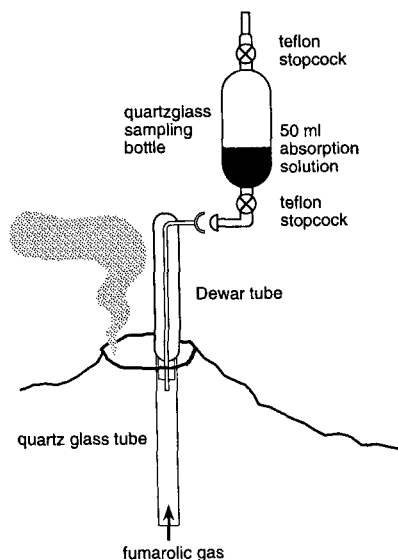


Fig. 2. Sampling setup for volcanic gases by absorption in alkaline solutions

Analysis

The TRIGA Mk II reactor of the Atominstitut der Österreichischen Universitäten (short irradiations) and the ASTRA reactor of the Austrian Forschungszentrum Seibersdorf were used for neutron irradiation of the samples. Depending on the nuclear properties of the collecting agents, two main irradiation schedules were applied: a short irradiation procedure and a longer one. For the short irradiation,

5 mL of the liquid solution were sealed into polyethylene capsules and irradiated for 10 minutes at a neutron flux of $ca\ 3 \cdot 10^{12}\ s^{-1}\ cm^{-2}$. After irradiation the solution was transferred into new vials for the measurement after a decay time of 15 min and a second run after about 24 hours. The elements Cl, Br, I, As, K and Na were determined. Short irradiations were not performed on the samples collected in NaOH solution because the activities of the short-lived activation products would be covered completely by the high activities of ^{24}Na .

To determine elements with long-lived activation products, an irradiation for 100 h in Seibersdorf at a neutron flux of about $6 \cdot 10^{13}\ s^{-1}\ cm^{-2}$ was applied. Because of the high temperatures due to gamma absorption during irradiation the samples must be sealed into Suprasil quartz glass vials, Furthermore, they must be dry and not contain any component that decomposes and leads to overpressure in the irradiation vial. This also rules out the irradiation of organic absorption media. Samples on activated charcoal were sealed directly into the irradiation vials while samples in NaOH

Table 2. Activation products, half-lives and gamma- energies used for gas analyses

Element	Activation product	Half-life	Gamma-energy, keV
As	^{76}As	26.30 h	559
Au	^{198}Au	64.72 h	412
Ba	^{131}Ba	11.81 d	496
Br	^{82}Br	35.28 h	777
Cl	^{38}Cl	37.30 min	2167
Co	^{60}Co	5.27 a	1173
Cr	^{51}Cr	27.70 d	320
Cs	^{134}Cs	2.06 a	796
Eu	^{152}Eu	12.70 a	1408
Fe	^{59}Fe	45.10 d	1099
Hf	^{181}Hf	42.50 d	482
Hg	^{203}Hg	46.59 d	279
I	^{128}I	24.98 min	443
K	^{42}K	12.36 h	1525
Na	^{24}Na	15.03 h	1368
Ni	^{58}Co	70.78 d	811
Rb	^{86}Rb	18.60 d	1077
Sb	^{124}Sb	60.20 d	1691
Sc	^{46}Sc	83.85 d	1121
Se	^{75}Se	120.37 d	265
Ta	^{182}Ta	115.00 d	1189
Te	^{131}I	8.04 d	364
Th	$^{233}Pa^{a1}$	27.40 d	312
Zn	^{65}Zn	243.75 d	1116
Zr	^{95}Zr	64.40 d	757

^{a1} ^{233}Pa is produced by the β -decay of ^{233}Th (half-life 22.3 min), formed by neutron capture of ^{232}Th .

Table 3. Blank values of absorption media for volcanic gases compared to the concentrations in an actual sample (fumarole GBC, sampling date 22 Jan. 1998). [AC] activated charcoal, [TRIS] tris(hydroxymethyl) aminomethane, $^7\text{LiOH}$, NaOH, NH_3 . All values in mg/kg (activated charcoal) or mg/L (4M solutions, ready for sampling)

	AC	TRIS	$^7\text{LiOH}$	NaOH	NH_3	actual sample
short activation						
As	3.2e-2	<2.4e-3	7.5e-3	-	<4e-4	6.9e-1±4e-2
Br	2e-2	3.2e-2	<7e-3	-	4.4e-3	1.01±0.06
Cl	42	1.7e-1	9.7e-1	-	3.9e-2	330±20
I	3.6e-2	8e-4	<6e-4	-	2e-4	2.7e-2±5e-3
K	n.d.	n.d.	n.d.	-	<4.4e-2	<0.1
Na	n.d.	1.92e-2	2.50	-	1.3e-2	7.7e-1±4e-2
long activation						
Au	n.d.	-	6e-5	3.5e-6	<2e-5	1e-5±6e-6
Ba	3	-	-	1.8e-2	2.6e-3	8e-3±3e-3
Co	0.2	-	-	1.1e-4	<6e-5	1.8e-4±1e-5
Cr	0.49	-	-	1.9e-2	2e-4	3.2e-2±2e-3
Cs	0.11	-	-	2.2e-5	4.6e-6	4e-5±2e-6
Eu	6e-3	-	-	3.5e-5	1.7e-6	<3.2e-6
Fe	169	-	-	4.9e-2	<1e-2	1.7e-1±9e-3
Hf	1e-2	-	-	7.4e-4	<3e-6	1.4e-4±7e-6
Hg	9e-3	-	2.8	1.3e-5	<2e-5	3.0e-4±3e-5
Ni	n.d.	-	-	1.1e-2	1e-3	1.2e-2±2e-3
Rb	9.8	-	-	7.6e-4	<4e-4	7.3e-4±2e-4
Sb	8e-3	-	0.24	4.2e-4	<8e-5	2.3e-3±1e-4
Sc	5.7e-2	-	-	1.1e-5	<1e-5	<1e-5
Se	5e-2	-	-	8.0e-5	<5.2e-5	2.3e-1±1e-2
Ta	<3e-3	-	9.5e-2	1.0e-5	<8e-6	<2e-5
Te	<5	-	-	1.0e-3	<1e-4	5.4e-3±5e-4
Th	<3e-2	-	-	2.2e-5	<2e-5	1.6e-4±2e-5
Zn	1.4	-	-	9.2e-3	6.2e-4	4.8e-2±2e-3
Zr	<2	-	-	3.4e-2	<1.5e-3	3.4e-3±2e-3

underwent a special neutralization and freeze drying procedure to meet the requirements [10]. Samples in NH_3 were pipetted directly into the irradiation vials and dried at 65° . This is sufficient to decompose $(\text{NH}_4)_2\text{CO}_3$, which would not withstand the irradiation. The samples were measured twice, after decay times of 3 days and 3 weeks, respectively. Samples in NaOH solutions were measured only after 3 weeks and total decay of ^{24}Na . A high purity germanium detector (100 cm^3 , 30% rel. efficiency), connected to a high-rate high-resolution gamma spectrometry system [12] was used for the measurements. Table 2 provides information about the activation products and the gamma-lines used for evaluation.

Table 4. Elements detectable by NAA in volcanic gases, collected by various absorption media.
 AC Activated Charcoal, TRIS Tris(hydroxymethyl) aminomethane, $^7\text{LiOH}$, NaOH, NH_3 .
 \oplus can be determined, – cannot be determined

element	AC	TRIS, $^7\text{LiOH}$	NaOH	NH_3
short activation				
As	\oplus	\oplus	–	\oplus
Br	\oplus	\oplus	–	\oplus
Cl	\oplus	\oplus	–	\oplus
I	\oplus	\oplus	–	\oplus
K	–	\oplus	–	\oplus
Na	–	\oplus	–	\oplus
long activation				
Au	–	–	\oplus	\oplus
Ba	–	–	–	\oplus
Cr	–	–	–	\oplus
Cs	–	–	–	\oplus
Fe	–	–	–	\oplus
Hf	–	–	–	\oplus
Hg	\oplus	–	\oplus	\oplus
Ni	–	–	–	\oplus
Rb	–	–	–	\oplus
Sb	\oplus	–	\oplus	\oplus
Se	\oplus	–	\oplus	\oplus
Te	\oplus	–	\oplus	\oplus
Th	–	–	–	\oplus
Zn	–	–	\oplus	\oplus
Zr	–	–	–	\oplus

3 Results

The sensitivity of trace element determinations in volcanic gases is mainly ruled by the concentrations of these elements in the absorption media. Elements that contribute significantly to the gamma background or show interferences with elements of interest must also be considered. Table 3 shows the concentrations of elements found in the absorption media with respect to the activation times applied. In addition, the values of an actual sample are listed. The elements that were therefore determined in the gas samples are given in Table 4. The blank values for the quartz glass vials used for long time activation were also determined. The results are given in Table 5.

4 Discussion

The applicability of a collecting agent for volcanic gases is governed by several considerations: Its sampling properties in the field, its suitability for precisely determining the quantity collected, its price and commercially available purity, and its irradiation properties.

Table 5. Concentrations of elements in quartz glass irradiation vials (mg/kg)

element	concentration	element	concentration
Au	$2.1e-6 \pm 5e-7$	Rb	$<1e-3$
Ba	$1.46e-3 \pm 5e-4$	Sb	$3.24e-4 \pm 2e-5$
Co	$3.57e-4 \pm 2e-5$	Sc	$1.54e-4 \pm 8e-6$
Cr	$2.62e-3 \pm 1e-4$	Se	$<7e-5$
Cs	$2.9e-5 \pm 9e-6$	Ta	$3.4e-5 \pm 1e-5$
Eu	$5.3e-6 \pm 1e-6$	Te	$<1.4e-4$
Fe	$1.96e-1 \pm 1e-2$	Th	$9.72e-5 \pm 1e-5$
Hf	$1.23e-3 \pm 6e-5$	Zn	$3.33e-3 \pm 1e-4$
Hg	$<4e-5$	Zr	$7.0e-2 \pm 7e-3$
Ni	$<2e-3$		

Activated Charcoal

The use of activated charcoal in an open system yields high volume samples and therefore high enrichment factors. The condensate has to be separated and the remaining gases have to be filtered again by an additional charcoal filter. All these components have to be analyzed separately. Nevertheless, some components like incondensable gases are lost and cannot be determined in the sample. Additional sampling and analyses are therefore required. Eight elements were determined in gas samples collected by this method.

Sodium Hydroxide

The conventional technique uses a NaOH solution. It is a cheap reagent with perfect sampling properties, available in high purity grades, but rules out the determination of Na in the gases and the use of short- and medium-lived activation products for NAA. A product for long irradiations can be prepared by neutralization and freeze drying. 6 to 8 elements can be determined depending on the purity of the reagent.

Lithium -7 Hydroxide

$^7\text{LiOH}$ was found to be highly contaminated by Hg and Ta and Sb. Purification processes were carried out successfully [8], but the price of the reagent and its poor commercial availability excluded further application.

Organic Absorption Solutions

Tris(hydroxymethyl)aminomethane offers perfect purity / price ratios, but the absorption velocity for CO_2 is much lower than that of all other reagents tested. Additionally, long irradiations cannot be applied for two reasons: drying at low temperatures such as freeze drying is not possible and gas production as a consequence of decomposition during irradiation must be expected. Tetraethylammoniumhydroxide shows perfect sampling properties but is not available in high purity grades.

Ammonia Solution

Diluted ammonia solution (10%) was tested and found extremely useful. Higher concentrations cannot be used for sampling because of the partial pressure of NH_3 which exceeds atmospheric pressure at slightly elevated temperatures, rendering gas absorption impossible. Both short and long irradiation times can be applied. At a temperature of 65° no loss of trace elements was observed. After evaporation of excess NH_3 , most of the volatile trace metals like Hg and Sb precipitate in the acidic solution as sulphides. NH_3 is commercially available or even prepared easily in highest purity grades by isothermal distillation. A combination with quartz glass sampling bottles yielded the most satisfactory results.

5 Conclusions

The application of a "closed system" offers better conditions for the determination of trace elements in volcanic gases than an open system despite being restricted to smaller samples. The use of NH_3 solution provides the optimum performance for sampling and irradiation. Quartz glass sampling bottles and the exclusive use of PE (polyethylene) and PTFE (Teflon, polytetrafluoroethylene) for preparation work are indispensable. The results obtained by the technique described contribute significantly to our knowledge about subsurface reactions and geothermal processes governing the fluid dynamics of a volcanic environment.

Acknowledgements

We wish to thank the reactor crews of the ASTRA Seibersdorf and the TRIGA MkII reactor at the Atominstitut Vienna for cooperation and the Gruppo Nazionale per la Vulcanologia, Italy, for financially supporting our work.

References

- [1] M. Martini, I. Giannini and B. Capaccioni: *Acta Vulcanologica* **1** (1991) 7.
- [2] G. Chiodini, R. Cioni and L. Marini: *Appl Geochem.* **8** (1993) 357.
- [3] R. Cioni and F. DeAmore: *Geothermics* **13** (1984) 375.
- [4] M. Carapezza, P. M. Nuccio and M. Valenza: *Bull. Volcanol.* **44** (1981) 547.
- [5] M. Bichler, R. Platschka and K. Poljanc: *J. Radioanal. Nucl. Chem.* **165** (1992) 61.
- [6] M. Bichler: *J. Radioanal. Nucl. Chem.* **166** (1992) 31.
- [7] M. Bichler, K. Poljanc and F. Sortino: *J. Radioanal. Nucl. Chem.* **192** (1995) 183.
- [8] M. Bichler and F. Sortino: *J. Radioanal. Nucl. Chem.* **199** (1995) 365.
- [9] M. Bichler and F. Sortino: *J. Trace and Microprobe techniques* **14** (1996) 275.
- [10] M. Bichler and F. Sortino: *Radiochimica Acta* **78** (1997) 177.
- [11] W. F. Giggenbach: *Bull. Volcanol.* **39** (1975) 132.
- [12] G. P. Westphal: *Nucl. Inst. and Meth.* **A299** (1990) 261.