Determination and comparison of acidic gas ratios at the Stromboli Volcano and Mount Etna obtained by various active alkaline traps

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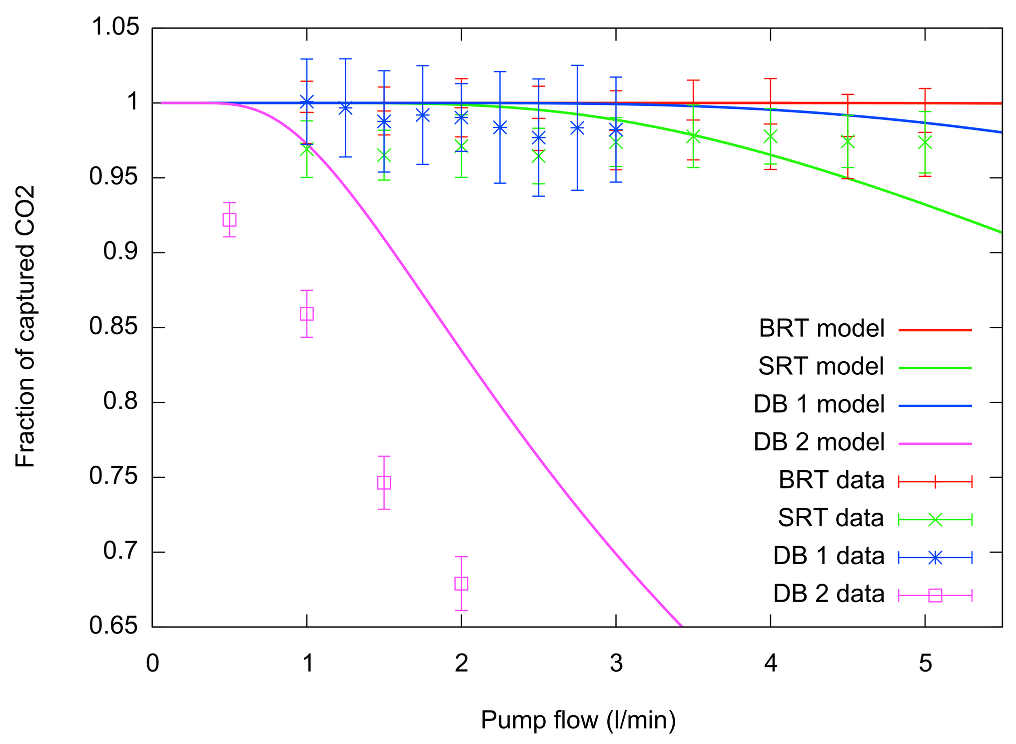
Introduction

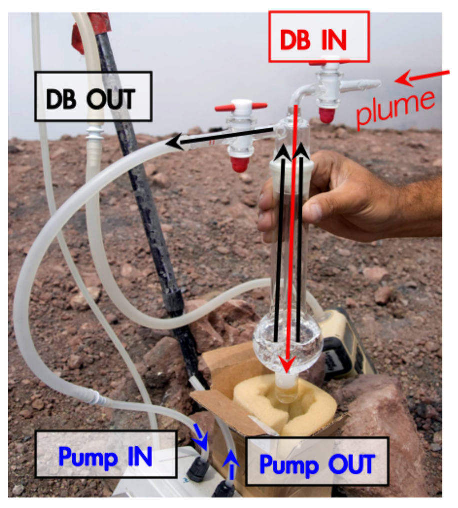
Determining volcanic gas composition helps to improve the understanding of the volcanic system, its effects on the atmosphere and the behavior inside the plumbing system. In-situ measurements are the basis for the monitoring of volcanic gas emissions, being complemented by remote sensing techniques over the last years. The application of established in-situ techniques to sample a diluted plume, still needs an increase in accuracy and a reduction of detection limits for most gases.

Sampling Efficiency



Fraction of captured CO_2 with respect to atmospheric concentration measured by commercial infrared gas analyzers for different pump flows. Additionally the theoretically determined absorption efficiencies for the instruments are plotted. The theoretical and experimental comparison of the DB to the modified RT resulted in a much higher efficiency for the latter.

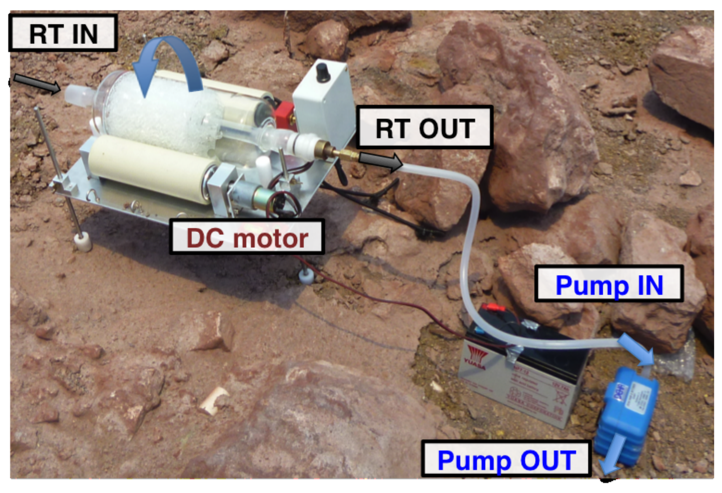
Sampling Techniques

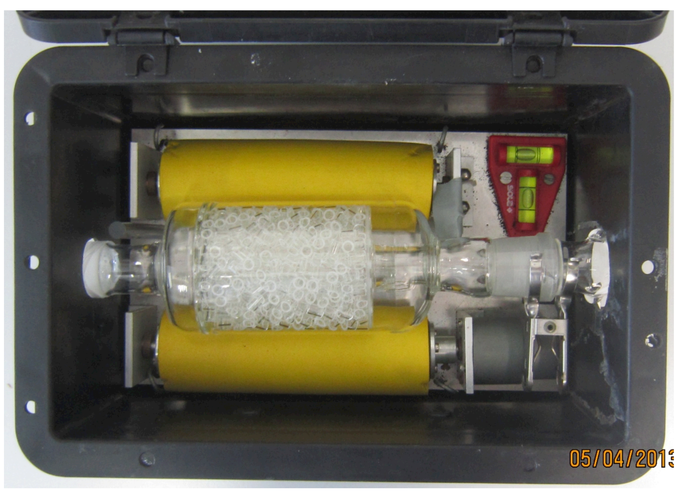


Drechsel bottle (DB)
Drechsel bottles are glassware which use a fritted glass piece fused to the tip of a gas-inlet tube reaching the bottom of the device. Having connected a air sampling pump, the frit creates small bubbles that allow an efficient diffusive transport of gas compounds into the solution (e.g. 100 ml of 1 M NaOH)

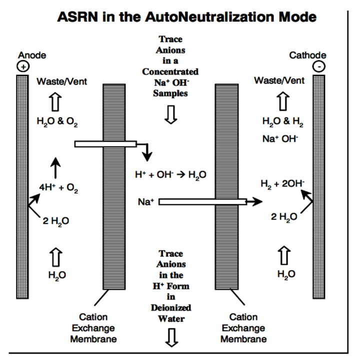
Filter pack (FP)
The active gas filtration method, so called "Filter pack", basically consists of several base impregnated filter papers clamped in series into a sealed filter holder system (sampling cassette) that can be connected to an air sampling pump. In this work three filter in a raw were used, impregnated by a 1 M $NaHCO_3$ solution with 10% glycerol .

Raschig-Tubes (RT)
The Raschig method is based on the creation of a huge interaction surface via humidification of many little glass rings with a 1 M NaOH solution by a constant rotation of the RT, containing these rings. Two types of RTs were assembled, a "big" one with 10 cm in diameter and 13 cm in length (BRT), and, due to the high efficiency, a "small" and easy portable one (SRT). The RTs provide high concentrations of dissolved species by using less sampling solution and the application of higher flow rates with respect to the DB. Simultaneous field sampling successfully attested up to 13 times higher molar concentrations and thus a higher sensitivity to detect less abundant species.





Sample Pretreatment

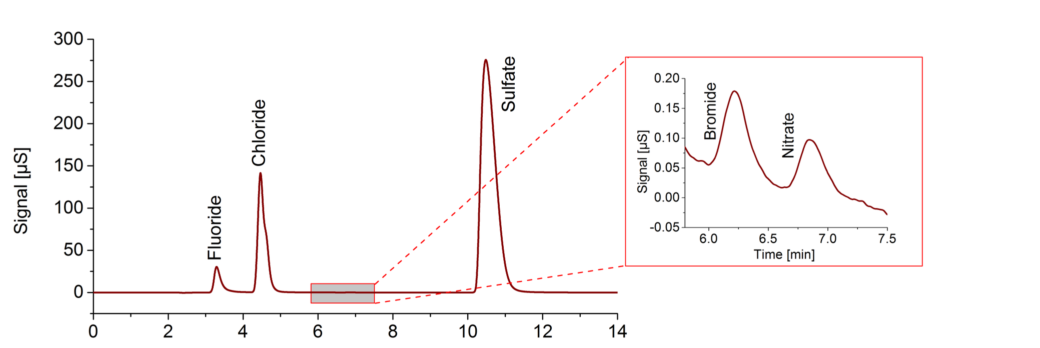


Adapted from Dionex Corporation ASRN 300 product manual

- Neutralization by ASRN 300 (Anion Self-Regenerating Neutralizer)
- Oxidation by H_2O_2
- Removal of H_2O_2 by MnO_2 powder
- Sonication
- pH adjustment

Analysis

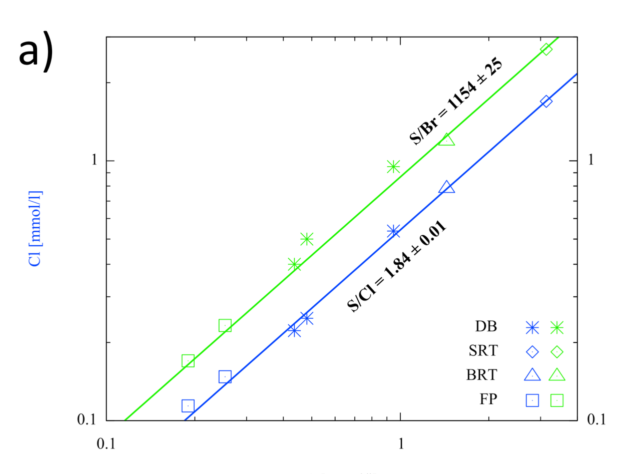
- Titration for dissolved CO_2
- Ion Chromatography (IC) for S, Cl, F, Br
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Br, I

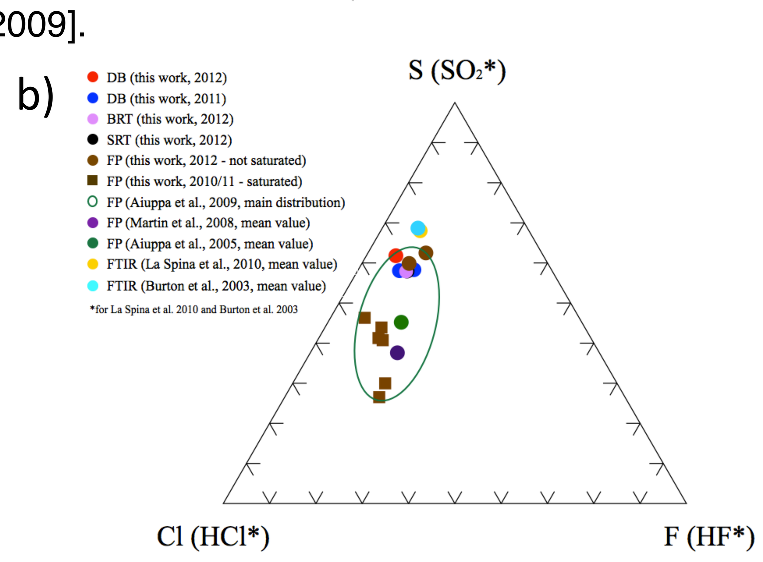


IC chromatogram of a NEC sample obtained by the SRT including all pretreatment steps

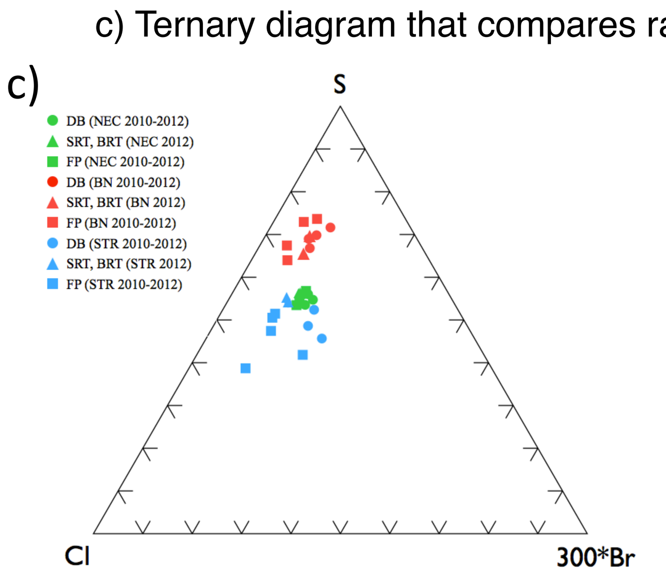
Results

a) Sulfur concentration versus chlorine (blue) and bromine (green) concentration measured in the sample solutions of NEC with linear regression (forced through 0).
b) Ternary diagram that compares ratios of sulfur, chlorine and fluorine for NEC samples analyzed in this work and published values from [La Spina et al., 2010], [Burton et al., 2003] and [Aiuppa et al., 2009].





c) Ternary diagram that compares ratios of sulfur, chlorine and bromine for samples analyzed in this work.



d)

	instrument	CO_2/S	S/Cl	S/F	S/Br	$S/I \cdot 10^4$
NEC	DB	6.7 ± 2.9	1.89 ± 0.07	7.0 ± 0.3	1015 ± 41	4.6 ± 0.2
NEC	SRT	3.6 ± 2.5	1.85 ± 0.08	5.4 ± 0.3	1167 ± 52	8.2 ± 0.4
NEC	BRT	7.5 ± 2.5	1.83 ± 0.08	5.5 ± 0.3	1206 ± 63	6.5 ± 0.4
NEC	FP	-	1.69 ± 0.08	6.4 ± 0.3	1102 ± 60	14.6 ± 2.5
BN	DB	26.7 ± 4.2	3.5 ± 0.1	81 ± 4	2000 ± 78	5.3 ± 0.3
BN	SRT	67.1 ± 7.4	2.6 ± 0.1	-	1925 ± 198	13.1 ± 2.5
BN	BRT	73.1 ± 8.1	3.2 ± 0.2	-	2217 ± 212	5.0 ± 0.2
BN	FP	-	2.7 ± 0.2	21 ± 3	2735 ± 357	14.5 ± 1.2
STR	DB	16.4 ± 17.9	1.59 ± 0.13	13 ± 1	673 ± 32	1.1 ± 0.1
STR	SRT	11.8 ± 21.1	1.61 ± 0.07	16 ± 1	1279 ± 68	7.6 ± 0.5
STR	FP	-	1.25 ± 0.06	-	1287 ± 77	28.4 ± 2.1

d) Mean volatile ratios and analytical uncertainties for the North-East (NEC) and the Bocca Nuova (BN) Crater at Mt. Etna and Stromboli's plume (STR). Samples from 2010 to 2012 were considered collected DB, SRT, BRT, and FP.

Conclusions

The results show that for most sulfur to halogen ratios the applied techniques are in good agreement. Up to 13 times higher analyte concentrations and thus more significant ratios were obtained by the RT with respect to the DB. Additionally, the optimization of the analytical procedure, including sample preparation and analysis by Titration, IC and ICP-MS led to a significant data set that covers a wide range of elements. In particular, less abundant species were quantified more accurately and iodine was detected for the first time in Stromboli's plume. Besides difficulties to determine fluorine, the FP technique turned out to be error-prone due to saturation effects.

Further Informations