Short Path Thermal Desorption - SPME - CT - GC/MS : Analysis of trace organic compounds present in hot volcanic gases with high sulfur, water and acid matrix

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The significance of organic emissions from quiescent volcanic degassing to stratospheric chemistry is that the negligible aqueous solubility of most emitted organic compounds does not lead to a quantitative tropospheric washout effect as postulated for explosive volcanic HCl and HF emissions. All previous attempts (eg. [1]) have two major analytical problems in common: a) loss and modification of compounds through photolysis, catalysis, adsorption, oxidation, & reaction with not separated condensate during sampling; b) insufficient chromatographic separation due to the high sulfur, water and mineral acid content of the gas. Sampling and analysis of organic compounds in hot (up to 900° C) volcanic gases therefore has to be customized to the difficult matrix of volcanic discharges.

We successfully developed and applied *Short-Path Thermal Desorption-Solid Phase Microextraction-Cryotrapping-GC-MS* (SPTD-SPME-CF-GC-MS) as a reliable standard protocol, together with new sampling techniques. It meets the required analytical accuracy and precision for reproducible (externally standardized) quantitative sampling and analysis.

Among the over 100 detected and quantified compounds are several alkanes, alkenes, arenes, phenols, furans, PAH's and their halogenated, methylated and sulfonated derivatives, and various heterocyclic compounds. All reported compounds are found well above laboratory, ambient air, adsorbent and field blank values. For some analytes (e.g., CFC-11, CH_2Cl_2 , CH_3Br),

concentrations are up to several orders of magnitude greater than even midlatitudional industrial urban air maxima.

[1] Jordan, A, Harnisch, J, Borchers, R, LeGuern, F, & Shinohara, H. (2000), "Volcanogenic Halocarbons" *Environ. Science Technol.* **34**(6):1122-1124.

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