



Fast and accurate both carbon and oxygen isotope determination in volcanic and urban gases using laser-based analyzer

Roberto M. R. Di Martino and Giorgio Capasso

Istituto Nazionale di Geofisica e Vulcanologia, sezione di Palermo, Palermo, Italy (robertomr.dimartino@gmail.com)

For decades, the measurements of carbon dioxide emission have been targeted to improve the accuracy of the estimate of the CO₂ budget from environmental systems and to reduce the gaps related to the carbon cycle effects on the Earth-climate. The main challenge was to identify the effective source of the CO₂ increase in the atmosphere.

The isotopic signature of CO₂ provides constraints on the carbon sources as well as on the exchanges between the carbon reservoirs and sinks. Among the techniques of volcano monitoring, the carbon isotope composition of the CO₂ ($\delta^{13}\text{C}(\text{CO}_2)$) has been largely used to discriminate and characterize the magmatic signature of the deep volcanic gases.

The development of a new optical class of isotope analyzer has allowed the in situ determination of the isotopic composition of some gas components in the air, when their concentrations are on the order of part per million by volume to several percent by volume. The availability of sophisticated and reliable instruments for measuring the carbon isotope composition of CO₂ has considerably increased the number of measurements, resulting in a significant increase in spatial coverage. At the same time, the relatively fast measurement procedures result in significant increases in temporal resolution. In addition, the technical development of compact instruments has enabled measurements to be conducted directly in the field with accuracies comparable to laboratory instruments. Finally, this new class of instruments provides very efficient measurements because no specific pre-treatments are required for the analytical sample.

Several urban areas are located close to gas sources which release significant amount of CO₂ and other toxic gases. They expose to hazard local inhabitants, especially where residential areas are located very close to emitting areas. Moreover, gas exhaust from vehicles or industries can contribute significantly to the full toxic gas concentration in the air in these areas. The latter kind of emissions has the carbon isotope composition of petroleum-related or methane-related combustion gases. Laser-based spectrometers, coupled with the monitoring of weather parameters, allow to differentiate anthropogenic from natural contributions at high temporal resolution (up to 1 Hz).

This work focuses on the development of a set of innovative, fast methods for directly determining in the field the stable isotope composition of carbon dioxide (carbon and oxygen) in the measurement conditions described as follows:

- dry gases discharged by soils having CO₂ concentrations from atmospheric to 100 Vol%;
- CO₂ in the atmosphere;
- dry gases collected in vials.

The methods have been applied using a laser based analyzer DeltaRayTM from Thermo Fisher. Several tests were performed in the laboratory in order to fine-tune each specific measurement method. The preliminary results of the tests performed in the field have been described. They show the reliability of the specific measurement method in different investigation settlements.