ISOTOPE ANALYSIS OF CARBON MONOXIDE IN ATMOSPHERIC SAMPLES

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A technique was established that allows the analysis of carbon and oxygen isotope composition of CO in small air samples (250ml). The method is based on the oxidation of CO to CO_2 with iodine pentoxide and the subsequent isotope analysis of CO_2. Potential applications include the use of CO and its isotopes as a tracer to distinguish different pollution sources.

1 INTRODUCTION

CO is produced in combustion processes, in particular during incomplete combustion, and in the atmosphere by the oxidation of methane and nonmethane hydrocarbons. In combination with NO_x it contributes to the ozone formation. The most important source of CO in Switzerland is the traffic. Since CO is emitted together with other air pollutants, it is a useful tracer for fossil fuel combustion. The consideration of stable isotopes in CO might help foster a better source apportionment. As another example, it might be possible to study the aging of polluted air masses because the removal of CO by OH radicals results in an isotopic depletion of the remaining CO.

2 EXPERIMENTAL

A method for the continuous-flow analysis of ^{13}C and ^{18}O of CO was recently published [1]. The technique is based on the oxidation of CO to CO_2 using the Schütze reagent, which consists of iodine pentoxide supported on silica gel. CO_2 is preferred as measuring gas because it can easily be cryo-focused with liquid nitrogen (LN_2; see Figure 1). This is necessary in order to first collect the small amount of CO (after conversion to CO_2) present in air samples, then release it in a short instant to produce a measurable peak size in the mass spectrometer.

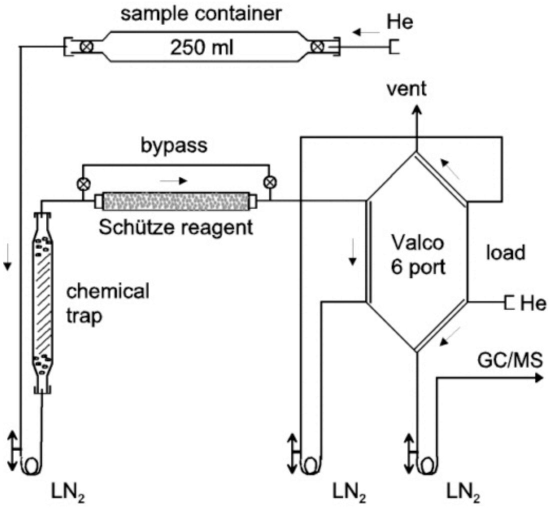

Fig. 1: Schematic outline of the preparation device for isotope analysis of CO. The first LN_2-trap and the chemical trap are designed to remove all of the CO_2 from the air sample. This is crucial as in the next step CO is oxidized to CO_2 with the Schütze reagent.

While the Schütze reagent adds an oxygen atom to CO, it does not alter the original oxygen isotope composition. It is possible to measure both isotopes on air samples of about 250ml with a CO concentration of 100ppb.

3 RESULTS

First results from car exhausts measurements are shown in Figure 2. Minor isotope fractionations are occurring in the first minutes after the engine of the vehicle was started. The $d^{13}C$-value probably reflects the isotopic composition of the gasoline, while $d^{18}O$ is approaching the value of atmospheric O_2 (23.5‰). In contrast, diesel engines are known to strongly fractionate the oxygen with $d^{18}O$ of CO being about 10‰ lower compared to O_2 [2]. Such differences might be useful for distinguishing different sources of CO in atmospheric air.

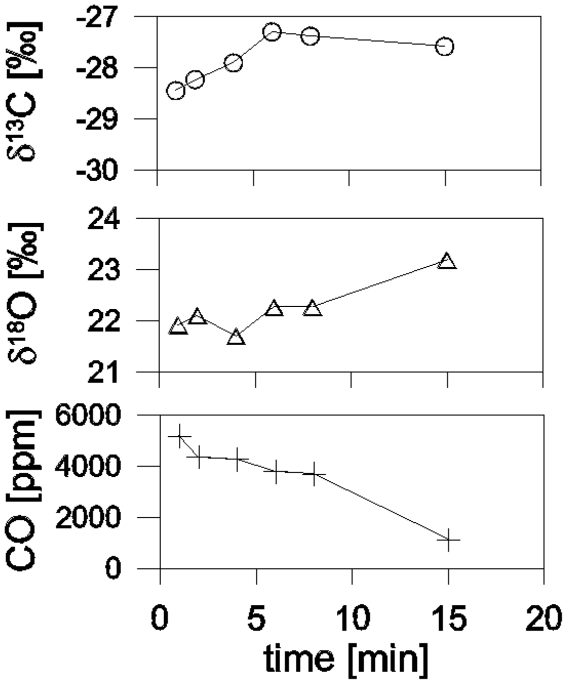

Fig. 2: Isotope and concentration measurements of CO from exhausts of a gasoline car. The time evolution after starting the cold engine is shown. The first 5 measurements were in neutral gear, the last one after a short drive.

4 REFERENCES

[2] S. Kato, H. Akimoto, M. Bräunlich, T. Röckmann, C.A.M. Brenninkmeijer, Geochem. J. **33**, 73 (1999).