Measurement of CH_3Cl in the atmosphere ◇

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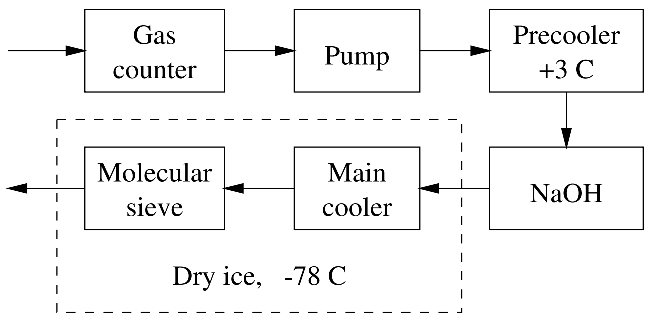
The long-lived radionuclide ^{36}Cl ($T_{1/2}$ = 301,000 y) is naturally produced in the atmosphere by cosmic ray induced nuclear reactions mainly on argon. Another source of ^{36}Cl is anthropogenic. The nuclear bomb tests caused a significant increase of ^{36}Cl in the atmosphere. Because of the relatively fast transport and fallout of chlorine in the atmosphere it was assumed that no evidence of bomb tests could be observed in modern precipitations. However the worldwide measurements of ^{36}Cl in rainwater discovered a large excess of ^{36}Cl relative to the theoretical calculation of natural production. This discrepancy can be explained if a part of bomb produced ^{36}Cl was integrated into another system (for example, biosphere), which allows the release of chlorine into the atmosphere. In this case the actual residence time of chlorine is extended that allows us to explain the measurements [1]. To check this hypothesis we are performing two types of experiments. One of them is measuring ^{36}Cl in lakes with long flushing times. Another one is the direct measurement of ^{36}Cl in methyl chloride, which is assumed to be the chemical form of ^{36}Cl reemitted from the biosphere into the atmosphere.

The concentration of methyl chloride in the atmosphere is not yet absolutely clear. Different sources show different values from 300 up to 1100 ppt although the average value seems to be about 550 ppt. If all organic chlorine-containing components are added about 10^3 m^3 of air have to be collected in order to obtain carrier free samples. Apparently this volume is too large to allow on-flow dissolving. So the first step was to collect (concentrate) the entire chlorine from this volume. The second step would be to make the final chemical preparation and to get a material, suitable for AMS-measurement (typically AgCl).

The collection of chlorine was achieved by using molecular sieve. About 85 g of the types 5A and 13X (Zeochem, Zurich, 3.3901.40.0 and 3.3901.41.0 correspondingly) were mixed in equal proportion, put into an U-shape stainless steel tube with a diameter of 16 mm and an overall length of 60 cm. After the filling of the tube, the molecular sieve was warmed up to 350°C in a vacuum oven for activation. After the cooling the oven was filled with N_2 and the tube was sealed.

The molecular sieve is able to catch and keep molecules with diameters of a few Å. In order not to have the molecular sieve overloaded we had to apply pre-filtering. The first step was on-flow pre-cooling down to a temperature of 3°C. It has allowed us to reduce the mass of water going through the system, and also of some organic acids and gases. The second step was the reduction of carbon dioxide, which was done pumping the air through sodium hydroxide (Merck, 1.01567.1000). It has also appeared to be an effective way to remove water from the air. Nevertheless there was too much water vapor left and we had to cool down to -78°C, this was achieved with dry ice. The dry ice was also used to cool the molecular sieve for an efficient capture of chlorine compounds.



The experiment was performed in Kranzberger Forst (10 km north of Freising) in a biological research station. The air was pumped with an average rate of 30 l/min. The pumped air volume was measured with a gas counter. Dry ice had to be refilled daily; the sodium hydroxide was changed every 3-4 days. The collection of methyl chloride took 17 days. 701 m^3 of air were pumped through the system.

The chemical preparation and the AMS measurement are under progress.

References

[1] C. Scheffel *et al.*, Geophys. Res. Lett. **26, 10** (1999) 1401

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