

## Instruments and Methods

# A new ice mill allows precise concentration determination of methane and most probably also other trace gases in the bubble air of very small ice samples

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**ABSTRACT.** A new extraction system has been constructed and tested which allows the extraction of gases from air bubbles in ice without melting it. An ice sample of up to 20 g is crushed in a sealed container by a milling cutter and the gas escaping from the opened bubbles is flushed with helium to a Porapak column where it is stored until its injection into the gas chromatograph. To avoid any contamination with CH<sub>4</sub> produced by friction in the gear section, a helium-flushed rotary feed-through is used. CH<sub>4</sub> analyses on ice samples of about 10 g from the last 1000 years give precise and reproducible results. In the future, it is planned to measure also the CO<sub>2</sub> and N<sub>2</sub>O concentrations on the same sample.

### INTRODUCTION

During the formation of glacier ice, air is separated from the atmosphere and enclosed in bubbles. At locations with a low mean annual air temperature, ice is formed by sintering of dry cold firn. In this case, the air in the bubbles has approximately the same composition as the air at the time of ice formation (Stauffer and Oeschger, 1985). To obtain information about ancient atmospheric compositions, air samples from ice formed in that epoch have to be extracted and analysed. Both steps, the extraction and the analyses of the air samples, need sophisticated methods. In this paper a new technique for extraction is discussed.

Air can be extracted by melting the ice under a vacuum and by collecting the escaping air by compression or condensation (Berner and others, 1980; Delmas and others, 1980; Craig and Chou, 1982; Rasmussen and Khalil, 1984). However, the meltwater can interact with the air and alter its composition. For CO<sub>2</sub> analyses, wet extraction is unsuitable. Therefore, several techniques for dry extraction have been suggested (Raynaud and others, 1982; Neftel and others, 1982; Barnola and others, 1983; Etheridge and others, 1988). In all cases, the ice sample is ground mechanically under a vacuum to small grains or powder and the escaping gas is either collected by compression or condensation, or it is flushed from the extraction compartment with an inert gas.

In our laboratory, we use a small crushing device for ice samples of about 20 g together with a laser absorption spectrometer to measure the CO<sub>2</sub> concentration (Zum-

brunn and others, 1982). A second dry-extraction device is a sort of ice mill for ice samples with a size of 500 g. It is mainly used for <sup>13</sup>C analyses on CO<sub>2</sub> extracted from ice (Moor and Stauffer, 1984).

For the CH<sub>4</sub> analyses, samples of several hundred grams of ice are either milled in the ice mill mentioned above or melted in a wet-extraction system. In both cases, the air is analysed by a gas chromatograph (Stauffer and others, 1985, 1988).

To determine CO<sub>2</sub> and CH<sub>4</sub> and probably N<sub>2</sub>O, on the same small sample of up to 20 g with a gas chromatograph, a new extraction method had to be developed. First, a chopper was built and tested; when in operation, it produced contaminating CH<sub>4</sub> and CO<sub>2</sub>. Finally, a machine which is more similar to our milling device but which is equipped with a helium-flushed rotary-motion feed-through worked without any CH<sub>4</sub> contamination. Before describing the latter system, we briefly discuss the chopping system, so that others may be aware of the contamination problems we have encountered with it.

### CH<sub>4</sub> CONTAMINATION IN THE CHOPPING DEVICE

From tests with the existing ice mill, we knew that friction between stainless steel and silver-coated stainless steel produces CH<sub>4</sub>. Because the new machine was planned to extract the air from small samples, any contamination had to be avoided and therefore the moving stainless-steel

surfaces were separated by rings made from polyoxymethylene (Delrin). In tests without ice and with constant milling frequency, the CH<sub>4</sub> contamination increased with the number of strokes and the CO<sub>2</sub> contamination increased with time and temperature.

Because gliding rings made from polyimide (Vespe) and brass also produced CH<sub>4</sub>, other pairs of materials were tested for contaminating under friction. But no combination of brass, chromium-plated brass and Plexiglas with brass, chromium-plated brass, copper,

aluminium, teflon-coated aluminium, polyoxymethylene and glass proved to be non-contaminating.

**THE PRINCIPLE OF A MILLING DEVICE WITH A HELIUM-FLUSHED ROTARY-MOTION FEED-THROUGH**

Each milling tool needs an axis which rotates in a bearing. Rotation in a bearing causes friction, and friction between the metals we tested or between those metals and synthetics causes methane contamination. Instead of trying to avoid this contamination, there is also the possibility of pumping away the methane. The milling tool is mounted on a very stable shaft. The shaft rotates at its other end in precision bearings. Between the milling tool and the bearings, the shaft rotates in a cylinder without touching its wall (Fig. 1). Helium is injected into the middle of this cylinder and flows between the cylinder and the shaft, partly in the direction of the bearings and partly in the direction of the compartment with the milling tool and the ice sample. The helium flowing towards the bearings is pumped away. The helium flowing through the sample compartment is used to flush the extracted air sample to the cryofocusing device. The principle of this system is very simple but the requirements in respect of precision and stability of the shaft and the bearings are difficult to attain. The clearance between shaft and cylinder should be narrow so that not too much helium is required. On the other hand, the shaft must not touch the wall of the cylinder if the ice sample is pressed against the milling tool.

The leakage rate of the helium-flushed rotary-motion feed-through, negligible in our system, is given by  $A_c v / [\exp(vd/K) - 1]$ ;  $A$ , cross-section of flow;  $c$ , concentration

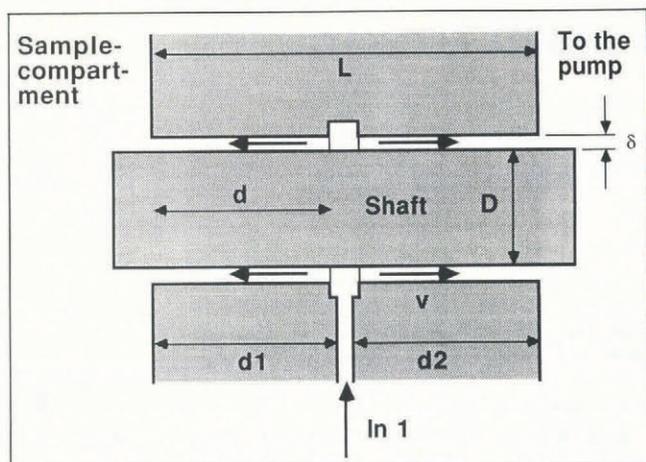


Fig. 1. Helium-flushed rotary-motion feed-through. The helium flow In1 (typically 200 ml min<sup>-1</sup>) branches along the shaft to the sample compartment and to the pump. Dimensions: L = 85.5 mm, d1 = 49.5 mm, d2 = 31 mm, D = 30 mm and δ = 0.085 mm. The location of Figure 1 in Figure 2 is indicated by the shaded area.

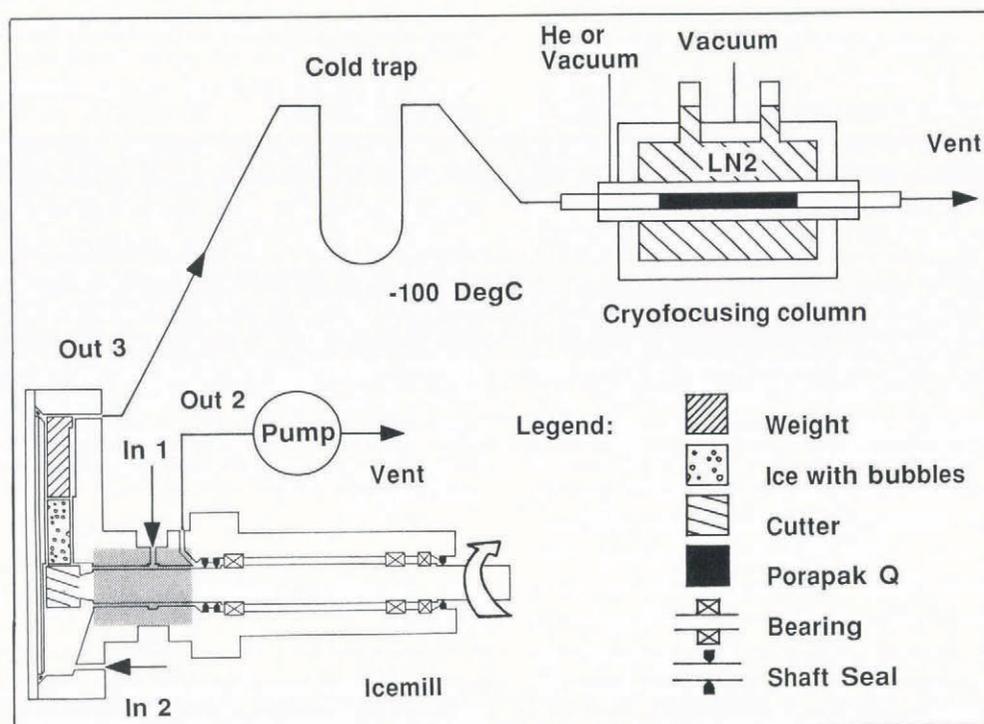


Fig. 2. Schematic arrangement of the ice mill, cold trap and cryofocusing column. The shaded area indicates the location of the helium-flushed rotary-motion feed-through (Fig. 1).

of gas;  $v$ , velocity of the helium flow;  $d$ , length of the seal;  $k$ , diffusion constant of the gas in the helium.

## DESCRIPTION OF THE MILLING DEVICE AND THE EXTRACTION PROCEDURE

The extraction system is schematically shown in Figure 2. It consists mainly of the milling device where the air escapes from the mechanically opened bubbles and a "cryofocusing" system where the air sample is collected and stored until its injection into the gas chromatograph.

The main parts of the milling device are the sample compartment with the milling cutter, the helium-flushed rotary feed-through and the bearing section. The sample compartment, made of stainless steel, is designed for ice samples up to a size of 20 mm × 20 mm × 60 mm. This amount of ice is needed in order to measure accurately not only the pre-industrial CH<sub>4</sub> concentrations but also the much lower concentrations during glacial periods. The ice is pressed against the milling cutter by its own weight and by an additional weight on top of the sample. The cutter is driven either by hand or a disc motor. The rotary-motion feed-through, made of stainless steel, has a length of 85.5 mm. The shaft has a diameter of 30 mm, the clearance between shaft and cylinder is 0.085 mm. The inlet for the helium is near the centre of the section. About 200 ml min<sup>-1</sup> helium (In1) are used, of which 100 ml min<sup>-1</sup> flow in the direction of the bearing section and prevent atmospheric air or any contamination produced in the bearing section from flowing or diffusing into the sample compartment. The flow in this branch of the feed-through section is controlled by a needle valve in the tube to the pump. The remaining 100 ml min<sup>-1</sup> of helium enter the sample compartment, adding to the 50 ml min<sup>-1</sup> helium of flow In2. Mixed with helium, the extracted air (or standard gas that was injected into flow In2 for calibration) passes via Out3 and the cold trap to the cryofocusing column.

The cryofocusing system consists of a stainless steel 75 mm × 2 mm i.d. Porapak Q column. The extracted air is collected at liquid-nitrogen temperature. At the beginning of the analysis, the Porapak Q column is switched to the carrier-gas flow of the gas chromatograph (7 ml min<sup>-1</sup>). There it is heated in less than 15 s to 85°C to release the air on to the separation column.

At the beginning of an extraction procedure, the ice sample is loaded into the sample compartment and the compartment is sealed. To remove the atmospheric air from the sample compartment, it is flushed for several minutes with helium at a very high flow rate. After this operation, carrier gas (purified helium with trace-gas impurities below our detection limits) passes through the system with the given flow rates, and the cryofocusing system collects possible impurities for 4 min. If no impurities can be detected, an amount of air similar to that expected to come from the sample with standard composition is inserted through tube In2. Then, the cryofocusing system collects again for 4 min. The analysis of the collected standard gas with the gas chromatograph serves as a calibration. Now, the ice sample is crushed and the escaping air is collected again for 4 min on the cryofocusing column and analysed with the gas chromatograph.

After the sample analysis, the measurement with standard gas is repeated. The frequency of the motor, as well as the duration of its operation, is held constant with all the samples of a series. A sample of 20 mm × 20 mm × 30 mm real ice is usually milled in 2 min at approximately 375 r.p.m. (cutter with six blades). The total time needed for the analysis of one ice sample, including loading of the sample, the different calibration measurements and the removal of the ice chips from the sample compartment, takes about 1 h.

## TEST RESULTS

The Porapak Q column was tested for its absorption capacities for the major air constituents and traces of CH<sub>4</sub> and CO<sub>2</sub>. It works well within the range of air amounts and trace concentrations expected in ice-age and Holocene ice samples if it is colder than -170°C.

The cold trap, held at -100°C, does not alter the air composition.

Tests on the ice mill have been made with pure single-crystal ice of a size up to 20 g. There was still a detectable contamination with CH<sub>4</sub> produced by the friction of the stainless-steel weight on top of the ice sample on the wall of the sample compartment. After the metal weight was replaced by one which is surrounded by single-crystal ice, the contamination by CH<sub>4</sub> was below the detection limit of 20 ppb.

To test the system as a whole, ice samples from Siple Station, West Antarctica, and Summit, Greenland (EUROCORE), were analysed. The measurements show that the reproducibility of the analyses is better than 15 ppb, which is better than any precision achieved previously (Rasmussen and Khalil, 1984; Stauffer and others, 1985, 1988; Raynaud and others, 1988; Chappelaz and others, 1990). However, there was a difference in the absolute CH<sub>4</sub>-concentration values compared to earlier measurements on larger samples (Stauffer and others, 1985), even though the same standard gas was used. The new measurements were between 50 and 100 ppb lower. Tests showed that this discrepancy originated from contamination of the standard gas for calibration when it was injected into the sample compartment. Notably, the operation of a few stainless steel valves in the inlet system produces a detectable CH<sub>4</sub> contamination. To avoid this source of contamination in the future, we shall install teflon-coated valves that are similar to those on the gas chromatograph and that have been proved to work.

The tests undertaken to prove the suitability of the new, small ice mill for CH<sub>4</sub> analyses are listed in Table 1.

CO<sub>2</sub> contamination in the order of several per cent is due to desorption of CO<sub>2</sub> from the walls of our system. It is larger than in our crushing system used with the laser absorption spectrometer because the milling and air-collection times are longer. The reproducibility of the CO<sub>2</sub>-concentration measurements is about 7 ppm and the mean value is about 10 ppm higher than that measured with the laser absorption spectrometer or the ice mill for 500 g samples and the gas chromatograph (Stauffer and Oeschger, 1985). If the sample compartment is cooled down to -40°C, the contamination decreases from 10 ppm

Table 1. Listed are the tests of the ice mill without those to test the weight that pushes the ice sample on to the milling cutter. They were undertaken to check the suitability of the new ice mill for CH<sub>4</sub> analyses. Milling of a piece of single-crystal ice takes longer than milling a piece of real ice having the same geometry. The samples of real ice are therefore contaminated with less than 20 ppb CH<sub>4</sub>. Every experiment with real ice consists of at least one blank measurement, two standard gas injections to calibrate and one run with milling of the sample

Experiment	Number of measurements	CH <sub>4</sub> ppb	Standard deviation ppb
1. Blank determination:			
(a) Without single crystal: 100 ml min <sup>-1</sup> and 50 ml min <sup>-1</sup> seal flow or nominal and half nominal pumping power, with and without cutter movement	Each combination at least once	< 20 (detection limit)	–
(b) With single crystal:			
No cutter movement	3	< 20	–
Milling of crystal	3	< 20	–
2. Real ice, 10 g samples:			
(a) Siple Station, 147.08 m:			
Yield not optimal	2	860.3	62.4
Yield O.K.	2	753.3	6.4
(b) EUROCORE			
Ten different depths	At least two per depth	*	10.9

\* To be published elsewhere.

to below the detection limit, which is about 0.3 ppm. Cooling of the mill (Ocampo and Klinger, 1982) and improvements in the cryofocusing device should result in better reproducibility. At present, the measurements of the CO<sub>2</sub> concentration in air extracted from ice samples of 20 g is more precise and faster by using our laser absorption spectrometer than with the gas chromatograph and the new extraction system. However, there is a considerable advantage by measuring several components on the same sample. Therefore, we shall still try to improve the precision of CO<sub>2</sub> measurement by using the new method.

Preliminary tests on N<sub>2</sub>O are promising and indicate that our system is also suitable for concentration measurements of this important atmospheric component (Zardini and others, 1989).

## FINAL REMARKS

The tests show that the new extraction device is well suited to measurements of the CH<sub>4</sub> concentration in air of ice samples of a size up to 20 g. The CO<sub>2</sub> and N<sub>2</sub>O concentrations are measured simultaneously but with less precision.

The cryofocusing device couples the mill to the gas chromatograph. A re-design of that device would allow use of the mill with gas-detection systems using no carrier gas.

## NOTES

Since the submission of this paper in 1991, the CH<sub>4</sub>-producing stainless-steel valves have been replaced and, after several tests that showed that the contamination had disappeared, the series of EUROCORE samples was re-measured. The new results confirm the precision achieved in the first series.

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