Instruments and Methods

A new device for the measurement of air content in polar ice

V. LIPENKOV,

Arctic and Antarctic Research Institute, 199397 St. Petersburg, Russia

F. CANDAUDAP, J. RAVOIRE, E. DULAC AND D. RAYNAUD

Laboratoire de Glaciologie et Géophysique de l'Environnement du C.N.R.S., 38402 Saint-Martin-d'Hères Cedex, France

ABSTRACT. A new device for measuring air content in polar ice has been designed, built and tested with 22 samples of Antarctic ice. The new technique is based on the barometric method which implies: (1) air extraction under vacuum by melting–refreezing of the ice sample placed in a calibrated cell, and (2) accurate air-pressure and temperature measurements. The new apparatus simplifies the experimental procedure, decreases the duration of measurement and can eventually be used in the field. It provides results with an accuracy equivalent to or better than other methods previously used.

INTRODUCTION

Measuring the total amount of air trapped by polar ice can provide valuable information on the atmospheric pressure prevailing during the time of ice formation and consequently on ice-sheet-elevation changes (Raynaud, 1983). The air-content profiles obtained along deep ice cores furthermore reflect a temporal variability of the ice porosity when the air bubbles close off. They may consequently also depend on other past climatic conditions such as wind speed and temperature, which influence ice sintering, and also the initial properties of snow (Martinerie and others, 1994).

Four different analytical methods have been used until now for measuring the air content in polar ice:

1. The first technique is based on gas extraction by ice melting under a liquid and air-volume measurement in a burette (Arnold-Alyabyev, 1930). The error of the method is considered to be as much as 5% (Langway, 1958) mainly due to uncertainties associated with the air dissolved in the meltwater. The liquid commonly used in this technique is kerosene (Langway, 1958) but air-saturated dimethyl silicone oil (Kameda and others, 1990a) and salt-saturated water (Lipenkov and others, 1993) have then been used to improve the precision of the measurements.

2. The second method consists of chromatographic air-peak measurements after the air has been extracted from the ice by its melting–refreezing under vacuum. This method has been implemented in parallel with methane-concentration measurements (Chappellaz, 1990). The absolute accuracy is estimated to be about 5% but the relative precision is better.

3. A barometric method of air-content measurements has been previously used along with a dry-extraction

procedure (Kameda and others 1990a). The total amount of air extracted by crushing the ice sample in a vacuum vessel of known volume was estimated with an accuracy better than 1% on the basis of precise air-pressure and temperature measurements. Nevertheless, the experimental error of the overall procedure may be significantly larger due to the limited efficiency of the crushing procedure in extracting all the air occluded in the ice (Raynaud and others, 1982).

4. The most accurate technique for air-content measurement has been developed on the basis of the vacuum-volumetric method (Raynaud and others, 1982). A glass vacuum line connected to a glass vessel containing the sample is used to extract air from the ice by melting–refreezing and to collect the air, after trapping the water vapor, in the burette of a Toepler pump for precise volume measurement under known room temperature and atmospheric pressure. The calibration tests performed by Martinerie (1990) and recently repeated during the present study have proved the absolute accuracy of the vacuum-volumetric method to be within ±1.5%. Average reproducibility of the method estimated by comparison between results obtained with two different extraction lines on ice samples cut from the same horizontal slice of ice core was found to be about ±0.7%. It is interesting to note that the same method has been used coupled with gas extraction by sublimation of ice instead of its melting–refreezing (Raynaud, 1977; Raynaud and others, 1982). A systematic overestimation of air content measured after the sublimation procedure may result from gas–solid interactions occurring during trapping of the water vapor (Raynaud and others, 1982).

Although the accuracy provided by the vacuum-

volumetric method is good enough for air-content measurements, the experimental procedure has several disadvantages (low productivity, the use of health-hazard products: mercury and phosphoric anhydride acid, the relative fragility of the glass extraction line, the need to use vacuum grease) which also cause difficulties in its application under field and laboratory conditions. Therefore, a new experimental technique has been developed.

Here, we describe the new apparatus for air-content measurement based on the barometric method. The sources of experimental uncertainties, absolute accuracy and reproducibility of the measurements are considered on the basis of theoretical calculations and experimental tests.

NATURAL VARIABILITY OF AIR CONTENT IN POLAR ICE

The air content V is commonly expressed as a volume $(cm^3 STP)$ of dry air in $1 g$ of ice reduced to standard conditions (STP: $T_s = 273 K$, $P_s = 1013 mbar$). The air content in polar ice ranges from 0.07 to $0.13 cm^3$ (STP) g^{-1} (Martinerie and others, 1992) due to the geographical and/or temporal variations of atmospheric pressure P_c (mbar), temperature T_c (K) and pore volume V_c (cm^3 g^{-1}) at the close-off depth in the ice sheet where the air becomes isolated from the atmosphere:

$$V = V_c \frac{P_c T_s}{P_s T_c} \quad \text{(Martinerie and others, 1992)}. \quad (1)$$

Overall variability of the air content, observed along deep ice cores recovered in Greenland and in Antarctica has an amplitude up to 25% (Budd and Morgan, 1977; Raynaud and others, 1979; Raynaud and Whillans, 1982; Herron and Langway, 1987; Kameda and others, 1990b; Lipenkov and others, 1993; Martinerie and others, 1994). On the one hand, this variability may reflect long-term variations in:

Elevation at which the air becomes trapped in the ice because of down-slope ice advection or changes in ice-sheet surface elevation (an elevation change of 50 m may generate a change of about 1% in air content).

Atmospheric pressure (about 7 mbar/1%).

Temperature (2°C/1%), including the temperature effect on close-off porosity.

On the other hand, an air-content signal with the same order of magnitude can be induced by variability of close-off porosity, V_c, associated with the stratigraphy of the ice sediments due to different weather conditions (causing very short-term variations within a few centimeters of ice core) or with wind-speed changes due to climatic variability (Martinerie and others, 1994). Investigation of the short-term V variations with respect to other structural properties of the ice provides experimental constraints for modeling the ice-sintering and air-trapping processes in ice sheets (Martinerie and others, 1992).

A common experimental uncertainty for all methods of air-content measurement is due to the so-called "cut-bubble effect" because some gas is lost when cutting air bubbles (or cavities formed from air-hydrate decomposition after ice relaxation) at the surface of the ice sample during its preparation. This effect can be estimated quantitatively below a certain depth in the ice sheet (5–10 m beneath close-off) where the shape of bubbles is simple enough for determination of their size. For ice samples of about 25 g, the correction of air-content measurements for the effect of cut bubbles varies from 10% near the close-off depth to 1% in the deeper strata (Martinerie and others, 1990). The corresponding uncertainty for air-content values may exceed 1.5% in the upper part of the experimental profile.

From all these considerations, an absolute precision of about 1% for the analytical technique itself seems to be appropriate with regard to the amplitudes of the V signal to be detected and to the "cut-bubble effect". In the following sections we focus the discussion on experimental uncertainties of the analytical procedure itself, based on the barometric method.

THE BAROMETRIC METHOD

Principle

The barometric method is based on the precise evaluation of the pressure P and temperature T of dry air extracted from an ice specimen by its melting–refreezing under a vacuum in a volume-calibrated cell. The real air sample contained in the cell is hereafter considered to be a mixture of two ideal gases: dry air and water vapor. Thus, if P_{meas} is the pressure measured in the cell, the pressure P of dry air will be given by:

$$P = P_{meas} - P_{H_2O} \quad (2)$$

where P_{H_2O} is the partial pressure of saturated water vapor at temperature T. Air content V of the ice is then obtained from the following relationship:

$$V = \frac{UPT_s}{M_i T P_s} \quad (3)$$

where M_i is the mass of the ice specimen and U is the volume occupied by the air sample in the cell and equal

$$U = U_{cal} - \frac{M_i}{\rho_i} \quad (4)$$

where U_{cal} is the volume of the calibrated cell while M_i/ρ_i represents the volume of the refrozen pure ice whose density, ρ_i, is mostly a function of its temperature (Bader, 1964).

A diagram of the measuring system is shown in Figure 1. An ice sample with known mass, M_i, is melted under a vacuum in cell 1 and then gradually refrozen by cooling the bottom of the cell to avoid air-bubble trapping during the freezing process. The cell and part of the line containing the extracted gas is immersed, before pressure measurement, in a liquid cryostat (shown in Figure 1 by the dotted square) to keep the air sample homogeneous at a low temperature T (−30°C). The low temperature
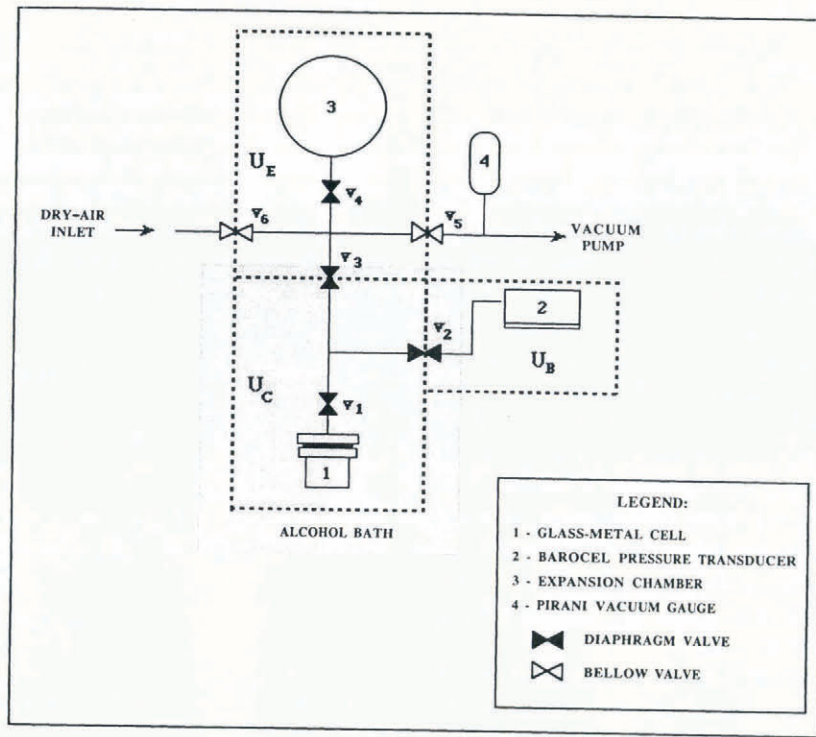
Fig. 1. Diagram of the measuring system.

ensures a minimum of water-vapor pressure P_{H_2O} in the line. The pressure P_{meas} of the gas is then measured with a type 590 Barocel (DATAMETRICS) pressure transducer (2 in Fig. 1).

The extraction line has three calibrated volumes U_C, U_B and U_E delimited in Figure 1 by dashed outlines. Volume U_C includes the volume of the empty cell plus the internal volumes of the valve v_1 and tubes up to the valves v_2 and v_3. Volume U_B is the sum of the internal volumes of the Barocel itself and fitting tube up to the valve v_2. The sum $U_C + U_B$ will allow us to calculate U_{cal}, the calibrated part of the line which is occupied by extracted gas and refrozen ice at the time of pressure measurement. Volume U_E is used only for self-calibration of the system. It includes expansion chamber 3 plus internal volumes of the valve v_4 and all fitting tubes up to the valves v_3, v_5 and v_6.

Optimum parameters of the measuring system

To estimate the accuracy of the experimental technique, we use the general equation relating the error ΔY of the function $Y = f(x_1, x_2, \cdots, x_n)$ to the individual errors Δx_i of the variables x_i, obtained from direct measurements

$$(\Delta Y)^2 = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i} \Delta x_i \right)^2. \tag{5}$$

According to Equation (5), the error of the air-content value determined from Equation (3) can be calculated as

$$\frac{\Delta V}{V} = \sqrt{\frac{(\Delta U)^2}{U^2} + \frac{(\Delta P)^2}{P^2} + \frac{(\Delta M_i)^2}{M_i^2} + \frac{(\Delta T)^2}{T^2}} \tag{6}$$

where ΔM_i and ΔT are the errors of sample mass and cryostat temperature (direct measurements), while ΔP and ΔU are the estimates of pressure P and volume U errors, obtained from Equations (2) and (4), respectively:

$$\Delta P = \sqrt{(\Delta P_{meas})^2 + (\Delta P_{H_2O})^2} \tag{7}$$

and

$$\Delta U = \sqrt{(\Delta U_{cal})^2 + \frac{(\Delta M_i)^2 + (M_i \Delta \rho_i / \rho_i)^2}{\rho_i^2}}. \tag{8}$$

If all individual errors are determined, the optimum ratio between sample mass, M_i, and cell volume, U_{cal}, for obtaining the best accuracy for air-content measurement can be evaluated on the basis of Equations (2)–(4) and (6)–(8). Assuming reasonable values and ranges: $V = 0.1\,cm^3\,(STP)\,g^{-1}$, $T = 240$–$255\,K$, $\Delta T = 0.1$–$0.3\,K$, $\Delta M_i = 0.01$–$0.03\,g$, $\Delta \rho_i = 10^{-4}$–$10^{-3}\,g\,cm^{-3}$, $\Delta P_{H_2O} = 0.01$–$0.03\,mbar$, $\Delta U_{cal} = 0.1$–$0.3\,cm^3$ and $\Delta P_{meas}/P_{meas} = 0.05\%$, we found that for samples of $M_i = 20$–$30\,g$ the best accuracy 0.2–0.3% of air-content measurement would be obtained with $U_{cal} = 100$–$400\,cm^3$. The pressure measured by the Barocel transducer would then be within the range 5–40 mbar. Taking into account that volume U_E should be about 10 times more than $(U_C + U_B)$ to maintain a similar pressure range during the calibration procedure, a pressure transducer with a full scale of 100 mbar and a main calibrated volume $(U_C + U_B) = 100$–$200\,cm^3$ are considered to be optimum for the measuring device. It is also shown in the next section that the limit of accuracy of 0.2–0.3% cannot be practically reached even with optimum parameters of the system because of uncertainties associated with the implementation of the method.

THE NEW TECHNIQUE

Description of the device

The vacuum line shown in Figure 1 is built using stainless steel tubing (6.35 mm) and CAJON VCR fittings. A diaphragm type of NUPRO valve is chosen for the valves v_{1-4}, because of its negligible change of internal volume between "close" and "open" positions, while NUPRO bellows valves are installed as $v_{5,6}$. The line can be evacuated by a turbo molecular pump backed by a rotary oil pump. A Pirani-type gauge is used for vacuum control.

The extraction cell is a glass–metal container. The bottom part of the cell is made of glass to allow observation of ice melting and refreezing, while its upper part and the lid are made of stainless steel. A copper "O" ring gasket is used to ensure good air-tightness between the cell and the lid, and to keep the cell volume as constant as possible during successive manipulations. The internal volume U_C of the empty cell and related tubing was designed to be about 137 cm^3.

The pressure transducer (type 590 Barocel) has a thermal base set at 40°C and measuring a pressure range up to 100 mbar. The pressure applied to its diaphragm is always maintained lower than 100 mbar to avoid hysteresis problems. The output signal is directly proportional to pressure and recorded by a DATA-METRICS-type 1450 pressure read-out. The accuracy of the transducer is about ±0.05% of the reading. The internal volume of the Barocel with no pressure applied is about 5.0 cm^3, while the diaphragm displacement under a pressure of 100 mbar can be as much as 0.16 cm^3. The volume U_B of the Barocel and the tubing up to valve v_2 is about 15 cm^3, so that the resultant volume $U_C + U_B \approx$ 152 cm^3.

The expansion chamber (3 in Fig. 1), which is made of stainless steel, has a lid for introducing a standard volume during the calibration procedure. The lid is coupled to the chamber with a copper "O" ring gasket. The internal volume U_E of the chamber, together with the related tubing (up to valves v_3, v_5 and v_6), is about 1363 cm^3.

The alcohol bath is cooled by a cryostat which maintains the temperature T at –30°C with a long-term temperature stability of ±0.05°C. The bath temperature is controlled by a high-quality stable platinum resistance thermometer. A good homogenization of 30 l of ethanol provides a ±0.01°C temperature uniformity.

Calibration procedure

The procedure for calibrating the volumes U_C, U_B and U_E is similar to that described by Schwander (1984). The calibration is carried out with the aid of two standard stainless steel volumes U_I (sphere) and U_{II} (cylinder) which have at 20°C the following characteristics:

$$U_I = 62.69 \text{ cm}^3 \ (\pm 0.02\%);$$
$$U_{II} = 524.20 \text{ cm}^3 \ (\pm 0.01\%).$$

The dry air at atmospheric pressure P_a is expanded from a volume U_C into pre-evacuated volumes U_E and U_B successively, and the resultant pressure in the manifold is measured with Barocel. The operation is repeated under three different conditions: (i) both volumes U_C and U_E are empty (the resultant pressure after expansion is P_1); (ii) volume U_C contains the standard solid volume $U_I(P_2)$; (iii) U_C contains U_I and U_E contains the standard volume $U_{II}(P_3)$. All parts of the line during the calibration are equilibrated at room temperature and pressure values $P_{1,2,3}$ are converted to 20°C. The atmospheric pressure is assumed to remain constant throughout the calibration time. From the above procedure, the volumes U_C and $(U_E + U_B)$, as well as atmospheric pressure P_a, can be obtained:

$$U_C = U_I P_1 F, \tag{9}$$

$$(U_E + U_B) = U_{II} P_3 F \frac{(P_1 - P_2)}{(P_3 - P_2)} \tag{10}$$

where $F = \dfrac{P_3 U_{II} + U_I(P_3 - P_2)}{P_1 U_I(P_3 - P_2) + P_3 U_{II}(P_1 - P_2)}$;

$$P_a = R P_1 \tag{11}$$

where $R = \dfrac{U_C + U_B + U_E}{U_C} = 1 + \dfrac{P_3 U_{II}(P_1 - P_2)}{P_1 U_I(P_3 - P_2)}$

is a dimensionless parameter of our system which allows calibration of the Barocel by adjusting the pressure P_1 read on the transducer in order to have P_a obtained from Equation (11) equal to the atmospheric pressure measured by a mercury barometer with an absolute precision of ±0.01%.

Volume U_B can be determined by expanding dry air at a pressure P_1 from U_B to the pre-evacuated volume U_C, containing the standard U_I. The resultant pressure P_4 allows us to calculate U_B:

$$U_B = (U_C - U_I)\frac{P_4}{(P_1 - P_4)}. \tag{12}$$

The measured pressures during the calibration procedure (P_{1-4}) are in the range 13–90 mbar. By applying Equation (5), the accuracy of the volume $(U_C + U_B)$ is ±0.15% and the absolute calibration of the Barocel has a precision of about ±0.2%.

Analytical procedure

A cubic ice sample of about 20–30 g (representing about 3 cm of ice-core thickness) is placed, after weighing, into the pre-cooled extraction cell. The extraction cell is then attached to the vacuum manifold with a CAJON VCR fitting welded to the lid of the cell. The cell is evacuated for 10 min with a turbo molecular pump. During pumping, approximately 1% of the ice is removed by sublimation from the sample surface. After pumping, the cell is isolated by closing stopcock v_1 and the bottom part of the flask is immersed for 10 min in an ultrasonic bath filled with warm water (50°C) to melt the ice. The experiments have demonstrated an efficiency of the ultrasonic bath in avoiding bubble formation during refreezing of the water. The ultrasonic bath is then replaced with the liquid cryostat and the bottom of the flask containing the melted water is immersed for 40 min

at $-30°C$. This results in gradual refreezing from the bottom of the cell. The refrozen ice is considered to be a polycrystalline bubble-free ice with a density of $\rho_i = 0.9207 \, \text{Mg m}^{-3}$ at $-30°C$ (Bader, 1964). The extraction cell and that part of the line representing almost all the volume $(U_C + U_B)$, except for the internal volume of the Barocel with its short connecting tubing, is then immersed in the alcohol bath as shown in Figure 1 by the dotted square. Valves v_1 and v_2 are opened to expand the air sample through the volume $(U_C + U_B)$. The extraction line is kept in the liquid cryostat for 30 min, allowing the air sample to equilibrate at $-30°C$ and to reduce the water-vapor pressure to 0.37–0.39 mbar. At the end of the procedure, the absolute pressure P_{meas} (range within 10–30 mbar) and temperature T (around 243 K) of the extracted air are measured with the Barocel and the platinum resistance, respectively.

The total duration of the analytical procedure is slightly more than 2 h. For comparison, the time efficiency of the vacuum-volumetric method described by Raynaud and others (1982) is about twice as slow.

Experimental uncertainties and corrections

In this section, we estimate the absolute precision of the air-content data obtained using the new technique, taking account of all possible sources of error and uncertainty associated with the calibration and analytical procedures described above. (The uncertainties due to cut-bubble effect are not considered here.)

An accuracy of about ± 0.01 mbar for P_{H_2O} evaluation is deduced from a comparison between the theoretical values and the direct measurements of water-vapor pressure using the Barocel, while the line containing an ice sample under vacuum was equilibrated at $-30°C$. Assuming $\Delta P_{meas}/P_{meas} = \pm 0.2\%$ after calibration of the Barocel, a resultant absolute precision for determining the dry air pressure P from Equation (2) is better than $\pm 0.25\%$.

The mass loss during the time of sample pre-evacuation was experimentally defined as 0.2 ± 0.1 g; therefore, the correction $\delta M_i = -0.2$ g must be applied to the measured sample mass and the resultant error $\Delta M_i/M_i = \pm 0.3$–0.5%.

To evaluate U_{cal} in Equation (4), a number of corrections have to be made to $(U_C + U_B)$ as deduced through the calibration procedure: (i) the thermal shrinkage of the given extraction line immersed in the alcohol bath at $-30°C$ with respect to its volume calibrated at $20°C$ is estimated to be $-0.2 \pm 0.01 \, \text{cm}^3$; (ii) the correction for the effect of the Barocel thermal base ($40°C$) during the calibration is $0.35 \pm 0.02 \, \text{cm}^3$; (iii) the effect of the temperature difference between the part of the extraction line immersed in the alcohol bath ($-30°C$), the short manifold exposed to the room temperature and the internal volume of Barocel ($40°C$) during the analytical procedure can be expressed as an apparent change of the volume $(U_C + U_B)$ which corresponds to a correction of $-1.9 \pm 0.1 \, \text{cm}^3$; (iv) the effect of the Barocel diaphragm displacement, which is considered to be a linear function of the applied pressure, can be eliminated by an average volume correction of $-0.13 \pm 0.02 \, \text{cm}^3$ (an estimate based on the difference

between pressure measured in the course of the calibration and analytical procedures). Adding together these different uncertainties, the total volume correction δU is $-1.9 \pm 0.1 \, \text{cm}^3$. This leads to $U_{cal} = U_C + U_B - 1.9 \, \text{cm}^3$ with an absolute accuracy of $\pm 0.25 \, \text{cm}^3$. As the density of refrozen ice in the extraction cell during our experiments was always the same as the density of pure ice within $\Delta \rho_i = \pm 0.002 \, \text{Mg m}^{-3}$, one can estimate, using Equations (4) and (5), the resultant error of the air-sample volume is $\Delta U/U = \pm 0.2\%$.

Finally, taking $\Delta T/T \leq 0.05\%$, after calibration of the platinum resistance in the alcohol bath, we can calculate using Equation (6) an overall error $\Delta V/V = 0.6\%$ for absolute air-content values obtained using the new technique. The calculations made by using an overestimating approach, assuming $\Delta Y = \sum |\frac{\partial f}{\partial x_i} \Delta x_i|$ instead of Equation (5) would lead to $\Delta V/V \approx 1\%$.

EXPERIMENTAL TESTS WITH ICE-CORE SAMPLES

Ice cores from two boreholes drilled in East Antarctica, 100 and 400 km inland from Mirnyy Station were used for the experimental tests. The two ice-core increments were collected from depths around 100 m (borehole at 100 km) and 124 m (400 km). In total, 22 cubic specimens of about 25–30 g have been prepared and measured for air content using the new apparatus and 11 samples using the old volumetric technique. The experimental results, not corrected for the cut-bubble effect, are given in Table 1, columns 3 and 4.

To estimate the reproducibility of the new analytical procedure, the air-content values obtained using the barometric method for two or three samples cut from the same horizontal slices have been compared (see column 6 in Table 1). The reproducibility, expressed as a relative difference between maximum and mean values for the same slices, was found to be not worse than $\pm 1\%$. The average reproducibility is $\pm 0.45\%$.

For inter-calibration between the two different analytical techniques, ten couples of adjacent ice samples of equal sizes cut from ten horizontal 3 cm thick slices of the ice core were chosen. One sample from each couple was measured for air content using the previous volumetric technique and the other using the new barometric technique. Apart from an abnormal case (slice 124.31 m in the ice core from 400 km), which gives a difference of 3.7%, the difference between V values measured by the two methods varies from 0.1 to 1.7%. This range can be explained by errors of ± 1.5 and $\pm 0.6\%$ quoted for the volumetric and barometric methods, respectively. An average value of the differences is equal to -0.23% when nine slices are taken into account (without slice 124.31 m) and to $+0.16\%$ for all studied slices. Therefore, our results indicate no systematic difference between the two analytical techniques.

CONCLUSION

A new device based on a barometric method of air-content measurements in polar ice has been designed for

Table 1. *Results of air-content measurements[*] in Antarctic ice using volumetric and barometric methods*

Drilling site	Depth of the slice bottom	Volumetric method V_v	Barometric method V_b	Mean value (barometric) V^*_b	Reproducibility (barometric) $[V_b(\max) - V^*_b]/V^*_b$	Difference between the two methods $(V_v - V^*_b)/V^*_b$
km	m	$cm^3 g^{-1}$	$cm^3 g^{-1}$	$cm^3 g^{-1}$	%	%
1	2	3	4	5	6	7
100	100.12	0.1163	0.1160 0.1154	0.1157	0.3	0.5
100	100.35	0.1162	0.1163 0.1173	0.1168	0.4	−0.5
100	100.38	0.1151	0.1140 0.1157 0.1164	0.1154	0.9	−0.3
100	100.41	0.1149	0.1164 0.1164	0.1164	0.0	−1.3
100	100.44	0.1150	0.1167 0.1173	0.1170	0.3	−1.7
100	100.47	0.1133	0.1133 0.1131	0.1132	0.1	0.1
100	100.53	0.1141 0.1139	0.1133 0.1156 0.1145	0.1145	1.0	−0.4
400	124.31	0.0931	0.0890 0.0905	0.0898	0.8	3.7
400	124.35	0.0888	0.0874 0.0875	0.0874	0.1	1.6
400	124.58	0.0937	0.0932 0.0944	0.0938	0.6	−0.1

[*] The results are not corrected for the effect of cut bubbles.

field and laboratory use. The absolute precision of the analytical technique has been estimated a priori and then checked experimentally to be within $\pm 0.6\%$. An average experimental reproducibility of the new method is found to be better than $\pm 0.5\%$. The duration of a single analytical procedure is about 2 h, i.e. half that of the previously used volumetric method. Another advantage of the new device, in addition to the high reliability of the stainless-steel extraction line, is that all health-hazardous products (mercury and phosphoric anhydride acid) used in the previous apparatus, have been eliminated.

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