

PRELIMINARY REPORT ON THE CONTAMINATION CONTROL FOR CHEMICAL ANALYSES OF ANTARCTIC ICE SAMPLES

Satoru KANAMORI¹, Nobuko KANAMORI¹, Kazuo OSADA¹, Eriko ISA¹,
Masataka NISHIKAWA², Okitsugu WATANABE³
and Fumihiko NISHIO³

¹*Water Research Institute, Nagoya University, Furo-cho,
Chikusa-ku, Nagoya 464*

²*National Institute for Environmental Studies, Yatabe-machi,
Tsukuba-gun, Ibaraki 305*

³*National Institute of Polar Research, 9–10, Kaga 1-chome,
Itabashi-ku, Tokyo 173*

Abstract: A possible penetration of contamination from the surface toward the inner part of cored ice and firn block samples was investigated for proper chemical analysis of Cl, SO₄, NO₃, NH₄, Na, K, Mg, Al, Fe, Ni, Cu, Zn and other elements. Generally, the contamination of the ice core sample remains within 10 mm under the surface. However, for the elements with intense contamination, a high concentration level in the surface layer tends to affect the level in the inner part. For the firn block sample, though the contamination by Cl, SO₄ and NO₃ remains within 20 mm of depth from the surface, NH₄, Na, K, Cu and Zn seem to pass through the surface layer but remain within 40 mm.

A thermal knife was constructed, for use in the laboratory, of nichrome wire of 1 mm diameter covered with a platinum pipe, tested for cutting cored ice samples and was found satisfactory without significant contamination of the elements listed above. The use of a stainless steel hand saw was also found practical for firn block samples.

1. Introduction

The glaciological group of the Japanese Antarctic Research Expedition (JARE) carried out the Ice Coring Project at Mizuho Station in 1983–1984 as a main project of East Queen Maud Land Glaciological Program and succeeded in coring down to 700.56 m below the snow surface. The ice core samples will be eventually opened to the public for glaciological study and also for general geoscientific study, especially for studies on changes in global environment. The purpose of the present study is to get basic informations needed for proper chemical analyses of micro-constituents contained in the samples of snow or firn block and cored ice, that is, to find how deep the surface contamination of samples reaches inside and also to find a reliable procedure for detaching contaminated parts from the samples.

Usually, the cutting of cored ice and firn block has been carried out by the use of a stainless steel band saw in a cold room kept at -20°C , where the atmosphere is apt to be very dry and dusty and the surface of the samples has a high possibility to suffer from contamination by dust. So, the sliced ice core is used in chemical analyses after

rinsing it with distilled water to melt and renew the surface. In the present study, a deep freezer was set in a class 100 clean room and cutting of the cored ice, 9 cm in diameter, was tried by the use of a newly developed thermal knife in it.

MUROZUMI *et al.* (1969) reported on the detailed technique to avoid even slight contamination of Pb during the ice block sampling. BOUTRON and PATTERSON (1983) also showed snow core contamination by Pb as a function of core radius. The Pb contamination was extending from the surface to a depth of 3 cm. In the present study, the depth of contaminated part from the surface was investigated for 17 elements as a basic information needed before starting chemical analyses.

2. Experimental

All processes for treatment of ice and firn samples and preparation of analytical solution were carried out in a class 100 clean room at Water Research Institute of Nagoya University.

2.1. *Cleaning of chemical wares*

Quartz and Teflon wares such as bottles, beakers and filtering devices were immersed into acetone, kept in hot concentrated nitric acid for several days, next in 3 M nitric acid prepared from ultra-pure nitric acid and Milli-Q water for 7 days, then in 0.2 M nitric acid prepared from ultra-pure nitric acid and Milli-Q water for 7 days and finally in Milli-Q water for more than 2 weeks.

Selected polyethylene wares (made of low density polyethylene) were immersed into acetone bath, kept in nitric acid (1+1) prepared from guaranteed quality nitric acid and Milli-Q water for several days and then processed according to the same procedure as given above except for the steps before concentrated nitric acid bathing.

2.2. *Reagents and filters*

Milli-Q water: Tap water was distilled in a stainless steel still and processed through Milli-Q system of Millipore Filter Corp.

Ultra-pure water: Milli-Q water was distilled twice under sub-boiling condition in a quartz still and stored in Teflon bottles.

Ultra-pure nitric acid: The commercial products of guaranteed quality were distilled twice under sub-boiling condition in a quartz retort and stored in Teflon bottles.

Membrane filters: Nuclepore filters with 0.2 μm pore size and 25 mm diameter were immersed into 2 M nitric acid prepared from ultra-pure nitric acid and ultra-pure water for 7 days and then rinsed and suspended in ultra-pure water for 7 days with renewing the water every day.

2.3. *Methods of analyses and associated instruments*

Cl, SO₄, NO₃, NH₄, Na and K: Ion chromatography (IC) by the use of Dionex Model 10 system.

Cu and Zn: HPLC method (KANAMORI *et al.* in preparation) using α , β , γ , δ -tetrakis (4-carboxyphenyl) porphine as a spectrophotometric reagent by the use of HPLC system Model 852 of Irika Instruments Inc.

Na, K, Mg, Ca, Al, Fe, Ni, Cu, Zn and other elements: ICP method by the use of Jarel Ash ICP Model 975.

2.4. Development of thermal knife for cutting ice core

A thermal knife was constructed from nichrome wire of 1 mm diameter inserted into a sheath of platinum pipe with 2 mm outside diameter and 1 mm inside diameter and fixed on a plastic support as illustrated in Fig. 1. Platinum was selected as the best metal among commercially available and chemically inert metals (Pt, Zr, Nb, Ta, Mo and W) because impurities of platinum (99.999%) are restricted to a few ppm amounts of Pt-group metals (Au, Ir, Pd and Rh), whereas the other metals contain not only the metals of the common group but also ppm amounts of Fe, Cr, Ni, and Cu, the contamination of which should be avoided because they attract our interest from the geochemical point of view.

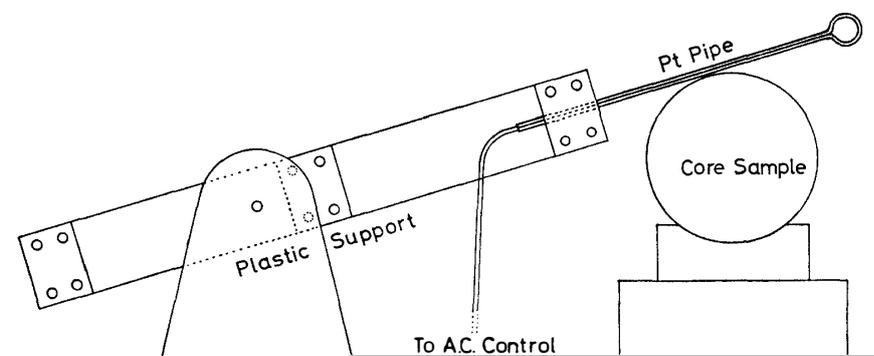


Fig. 1. Thermal knife for cutting ice core sample.

The platinum part of the knife was cleaned by immersing it into nitric acid (1+1) prepared from ultra-pure nitric acid and ultra-pure water and rinsed with ultra-pure water several times before use. The ice core sample was laid horizontally on a Teflon plate in the deep freezer kept at -30°C and the thermal knife was set on the core sample at a right angle to its axis. The temperature of the thermal knife was kept at *ca.* 70°C by controlling AC voltage through a transformer and it took *ca.* 30 min to cut it down. A sliced piece of 10 mm thick was easily obtained by the use of the thermal knife whereas the use of a hand saw was impossible because it would crack the ice sample into very small pieces. No contamination of the sliced sample was found by the elements tested. For firn block samples, while the thermal knife was effective for handling them, the use of a cleaned stainless steel hand saw was practical with no appreciable contamination and cracking.

2.5. Sampling

The ice sample was cored at Mizuho Station in June 1982 (Core No. 70A) by F. NISHIO and four members of the JARE-23. The sample was of solid ice with some air bubbles and 40 cm long with 9 cm diameter. It was wrapped with an aluminium foil, put into doubled polyethylene bags and placed in a carton box.

Firn block sample was taken with special care to avoid any contamination by K. OSADA of JARE-27 in February 1986. The sampling site was in a virgin space

located at *ca.* 500 m windward of Mizuho Station. Sampling was carried out with wearing clean cloth, clean cap, particle mask and polyethylene gloves keeping a down-wind position against the sample as much as possible. A $45 \times 35 \times 25$ cm block sample was cut out using a stainless steel hand saw. The cut block was wrapped with a cleaned polyethylene sheet, put into doubled polyethylene bags and kept in a carton box.

2.6. Pretreatment of sample

The ice core sample was cut at 30 mm from the upper end and then at 42 mm to get a sliced piece of 10 mm thick by the use of the newly developed thermal knife. Then successive marginal rings of the sliced piece were chiseled every 9 mm to be split into five portions from the surface toward the center by using a cleaned stainless steel chisel. The chips from each ring were gathered into each Teflon beaker, covered with a polyethylene film, left standing to melt away and used for analyses of Cl, SO₄, NO₃, NH₄, Na and K by the IC method as well as Cu and Zn by the HPLC method after filtration through a 0.2 μ m Nuclepore filter.

Another sample of 100 mm thick was also cut from the other end of the core sample. The successive marginal rings were chipped off every 11 mm by using the thermal knife to be divided into four portions. The melted samples were filtered and dried up by evaporation. The residues were dissolved into 1 ml of 1 M nitric acid and used for analyses of metallic elements by the ICP method.

The firn block sample was placed on a Teflon plate with the upper face upside, cut into two pieces at the center and one half of the sample was reserved for another use. All the faces except a vertical one of the block were cut off at 40 mm from the margin to avoid contamination from old faces. The remaining block was sliced every 20 mm in parallel with the reserved vertical face. Each slice was put into a Teflon beaker, covered with a polyethylene film, left standing to melt into water, filtered through 0.2 μ m Nuclepore filter and used for analyses by the IC, HPLC and ICP methods. A cleaned stainless steel hand saw was used throughout the processing.

3. Results and Discussion

The distribution of Cl, SO₄, NO₃, NH₄, Na and K measured by the IC method from the surface to the center of the ice core sample is shown in Fig. 2. The concentration levels of NO₃ and SO₄ in the outermost layer are apparently higher than the constant levels within the inner layers and suggest that a minor surface contamination remains on the surface. On the other hand, for Na and Cl, the difference between surface and inner constant levels is pronounced and still recognizable in the second layer. The facts that the amounts of the surplus Na and Cl over the inner layer are nearly equivalent and also that NH₄ behaves in the same manner suggest a possible minor contamination of the second layer during the sampling or pretreatment by some unknown source. Further studies are needed to understand the mechanism of contamination of the second layer. K shows the similar trend.

The distribution of Cu and Zn in the same sample measured by the HPLC method is shown in Fig. 3. The contaminations by these elements are evident in the outermost layer of the core sample and, for Cu, the inner four layers are left practically

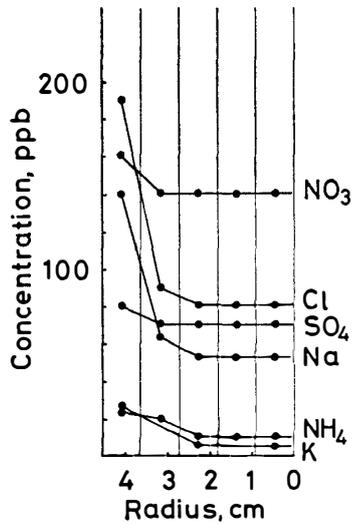


Fig. 2. Distribution of Cl, SO₄, NO₃, NH₄, Na and K in the ice core sample as a function of core radius.

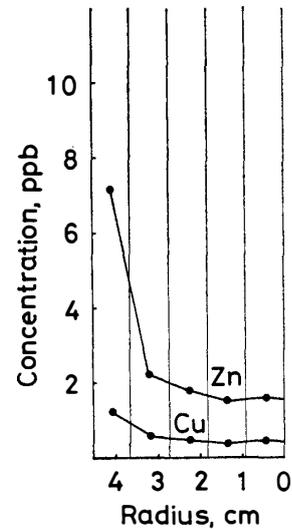


Fig. 3. Distribution of Cu and Zn in the ice core sample as a function of core radius.

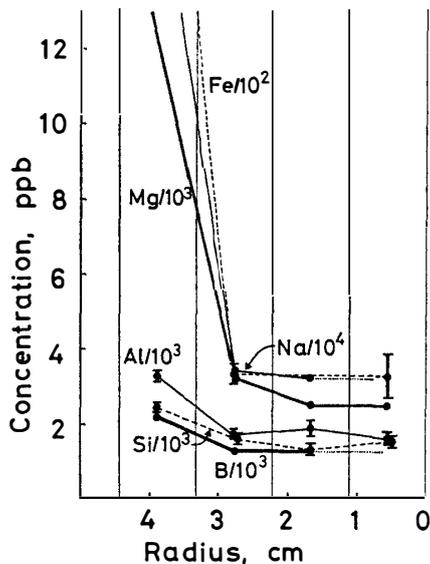


Fig. 4. Distribution of B, Si, Na, Mg, Al and Fe in the ice core sample as a function of core radius.

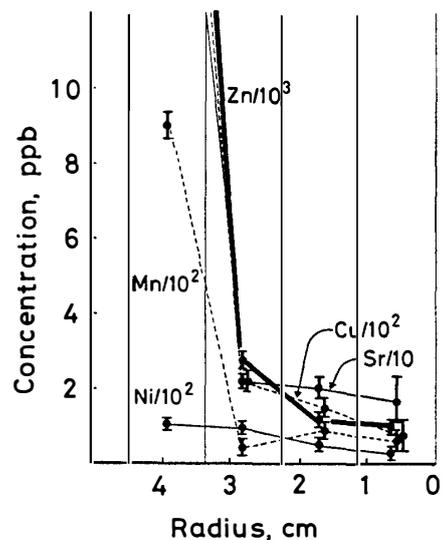


Fig. 5. Distribution of Mn, Ni, Cu, Zn and Sr in the ice core sample as a function of core radius.

uncontaminated whereas, for Zn, the level in the second layer is slightly but apparently higher than those in the inner layers.

The distribution of metal elements was studied also on another 10 cm thick sample. The sample was divided into four successive portions, the amounts of melt water ranged from 178 ml to 71 ml, and they were condensed to 1 ml by evaporation for analyses by the ICP method. The results are shown in Figs. 4 and 5, in which the possible error was indicated by the length of bar with a point for measured value.

Figure 4 shows the distribution of B, Na, Mg, Al, Fe and Si. High contamina-

tion by Na, Mg, and Fe at the surface is evident whereas that by B, Al and Si is not so high. All elements except Mg show that the contamination remains within the surface layer, possibly at the surface, when the analytical error is taken into consideration. However, that of Mg can be identified in the second layer (11–22 mm from the surface). The results by the ICP method are not the same as those by the IC and HPLC methods, and this seems to be due partly to the use of samples at different levels of surface contamination.

The distribution of Zn, Cu, Ni, Mn and Sr is shown in Fig. 5. Cu, Zn and Sr show very high surface contamination and, for Cu and Zn, the higher concentrations are observed also in the second layer. The contamination by Mn and Ni looks remaining within the surface layer if the possible analytical errors are considered. Of the other elements measured, 2.9 ppb of Pb, 0.17 ppb of Cd, 0.43 ppb of Cr and 76 ppt of Ti were found in the surface layer but they were under detection limit (Pb: ± 0.3 ppb, Cd: ± 0.01 ppb, Cr: ± 0.03 ppb and Ti: ± 10 ppt) in the inner layers. The contamination by these elements also seems to be limited on the surface.

The distribution of minor elements in the firn block sampled with special effort to avoid contamination was measured as a function of the depth from the reserved vertical face. Figure 6 shows the distribution of Cl, SO₄, NO₃, NH₄, Na and K. The

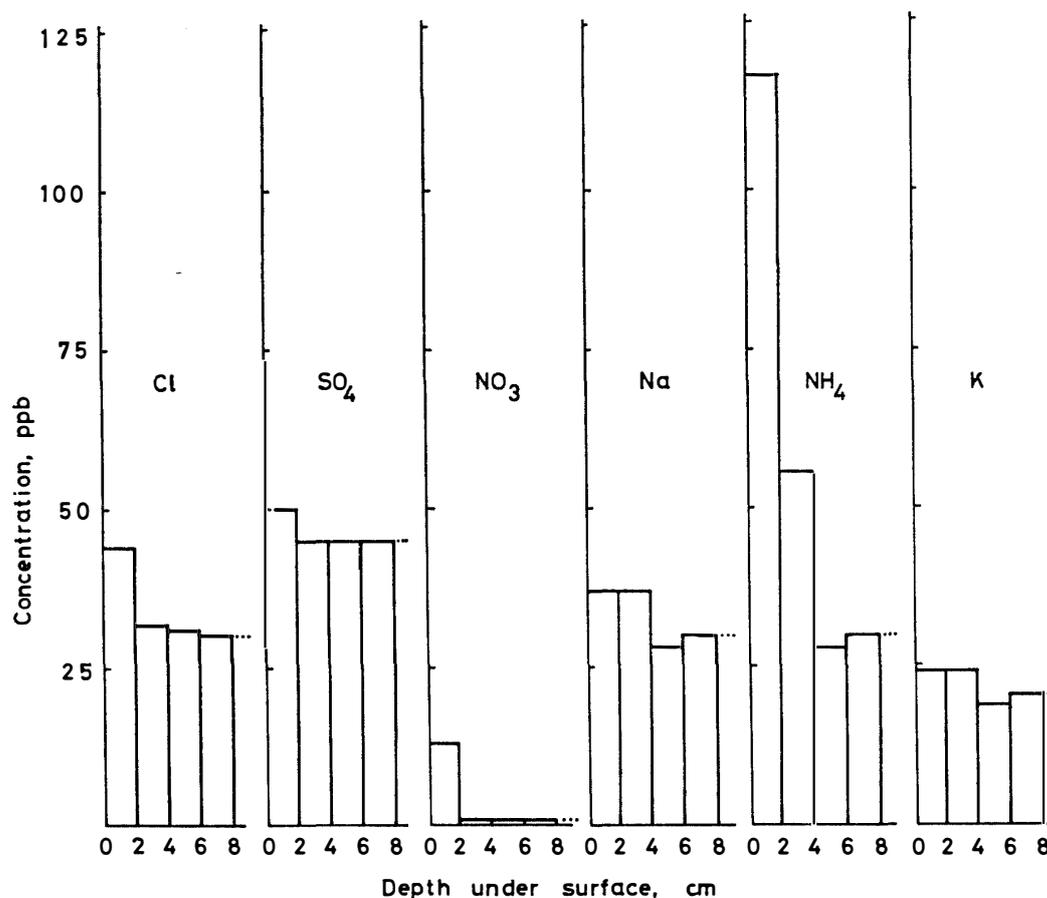


Fig. 6. Distribution of Cl, SO₄, NO₃, NH₄, Na and K in the firn block sample as a function of the depth under the surface.

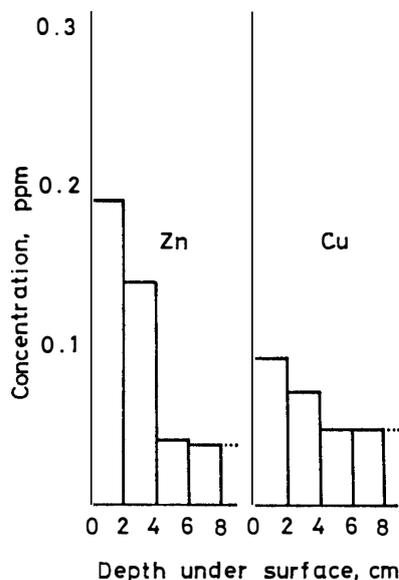


Fig. 7. Distribution of Cu and Zn in the firn block sample as a function of the depth under the surface.

surface contamination is highest by NH_4 and it is still apparent in the second layer. Though the levels of the surface contamination by Na and K are not pronounced, their levels in the second layer are higher than those in the inner layers. The surface contamination by Cl, SO_4 , and NO_3 is minor and looks remaining within the surface layer or probably on the surface.

The results given above indicate that, for some elements, the contamination is limited within the outermost layer whereas, for other elements, it penetrates through the 10–20 mm layer from the surface and can be identified in the second layer, the mechanism of which remains to be studied. The possibility that the deep contamination can be avoided by more careful processing will be discussed in a separate report.

Figure 7 shows the distribution of Cu and Zn. The concentration levels of these elements are apparently high within the successive two layers from the surface and suggest the ease of penetration into porous block sample reflecting the presence of these elements in a finely dispersed state in the air.

4. Conclusion

1) The thermal knife, made of nichrome wire with a platinum sheath, is satisfactorily used for cutting under the contamination-free condition of the core sample from the Antarctic ice sheet. A cleaned stainless steel hand saw is also useful for processing firn block samples. The use of a stainless steel chisel is practical for processing sliced core samples.

2) The successive marginal rings of 9–11 mm width were separated from a sliced sample to divide it into five or four portions. The analyses of them revealed that the contamination by NO_3 , SO_4 , Mn, Al, Si and B and possibly by Ti, Cr, Cd and Pb is limited within the outermost layer and that by Cl, NH_4 , Na, K, Mg, Fe,

Cu and Zn is often very high and extends to the second layer, the mechanism of which remains to be ascertained by further studies.

These results indicate that a careful treatment of the cored ice samples is needed to avoid surface contamination and that helps to protect the inner part against contamination.

In the firn block, sampled with special care to avoid contamination, Cl, SO₄, and NO₃ show relatively minor contamination in the surface layer (0–20 mm from the surface) and keep lower constant levels in the inner layers which suggests that the contamination is possibly limited on the surface. On the other hand, NH₄, Na, K, Cu and Zn indicate that the surface contamination is extending to the second layer (20–40 mm from the surface), the mechanism of which also remains to be studied.

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