

Design, Performance tests and Application of Melting System for Trace Element Analysis in a Shallow Firm Cores

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1. Abstract

The melting system of ice core samples has been a useful decontamination device. However, it should be very cautious to remove some pollutants caused by ice core drilling in the outer surface of firm cores with typical melting system due to percolation effect of melted samples. In this study, as a major improvement, the melting head of the melting system was constructed with fluorinated ethylene propylene (FEP) coated Cu divided into two zones due to the physical characteristics of firm core and performance tests such as decontamination efficiency and procedural blanks were systematically conducted with the artificial ice core samples (a cross section of 3.2 cm x 3.2 cm, ~10 cm long). Quality of the measurement data was confirmed by analyzing a certified reference material (SLRSS5, 1643e for elements) and -52.3 ~ 27.5 % of relative errors. Ice core samples were efficiently decontaminated by the melting system, which was verified by the signal intensity ratio (S.I.R.) of melting samples from two zones of melting head. Especially, procedural blank tests indicated that the concentrations of elements in melted samples from inner zone of melting head were very comparable with those of elements in system blanks except for Cu. The melting system was rinsed with 0.1% HNO₃ (total 10 ml) in order to remove memory effects of elements between ice core samples melted in series. The inter-comparisons of conventional mechanical chiseling method and melting system using NEEF firm core (#144, #155) agreed well with experimental results except for Cu. Finally, this technique was applied for the measurement of elements in firm core samples (68.675 ~ 71.425 m) drilled at the NEEF site located at the north-western part in Greenland (77.45° N, 51.06° W, surface elevation 2450 m, mean annual temperature 29 °C, accumulation 0.22m ice equivalent per year).

Key words: Melting system, Decontamination, NEEF firm core, Trace element

2. Experimental Method

Melting Method of Ice Core

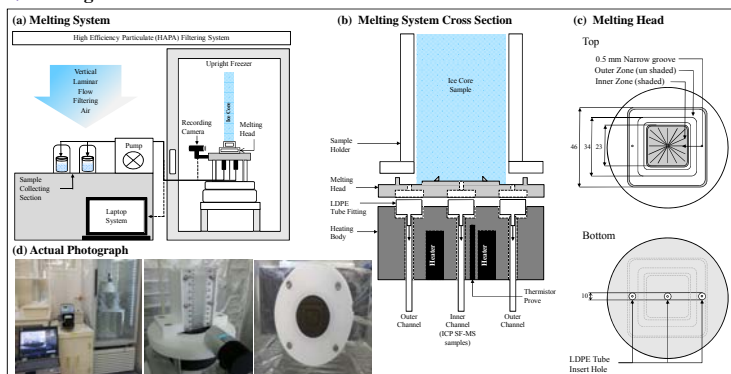


Figure 2. Schematic diagram of the melting system. (a) Melting system in upright freezer of clean booth (sample collecting section class - 10 and upright freezer class - 100); (b) Melting system cross section of the melting head assembly units; (c) Melting head; (d) Actual photograph of melting system.

Details of Melting System

Table 1. Specifications of Melting System

Components	Specifications
Melting Head	
- Material	Fluorinated ethylene propylene (FEP, 50 µm) coated Cu
- Zone	Two (inner and outer zones)
- Type	Rounded square type (inner - 23 mm, outer - 46 mm) Inner zone - Flat surface with narrow groove (0.5 mm) Outer zone - Layered flat surface (34 mm, height - 0.5 mm)
- Surface temp.	38 ± 2 °C
- Ice core section	(3.4 ± 0.2) × (3.4 ± 0.2) cm ² , 10 cm long
- Melting rate	Inner fraction: 2.56 to 3.42 ml min ⁻¹ Outer fraction: 1.56 to 2.08 ml min ⁻¹ Melting rate: 0.83 to 0.89 cm min ⁻¹
- Sample holder	Holder: fluorinated ethylene propylene (PTFE) Frame Scale: Transparent Polypropylene (PP)
- Fitting tubes	Tube E-Lab tube (Cole-Parmer, CP95608-44 and CP95608-36) Polytetrafluoroethylene (PTFE, Cole-Parmer, #06417-21) Fluorinated ethylene propylene (FEP, Cole-Parmer, #96005-06)
Heating Body	
- Material	Polytetrafluoroethylene (PTFE) coated Al alloy 6106
- Heat source of heating body	200 W Cu rod
Sampling Bottle	
- Material	LEPE wide mouth bottle (NALGENE, 30ml and 60ml)
- Cleaning Method	Nitric acid cleaning method (Hong et al., 2000)
- Distilled water	Milli-Q Academic system (Millipore, Milford, > 18.2 MΩ)

Chiseling Method of Ice Core

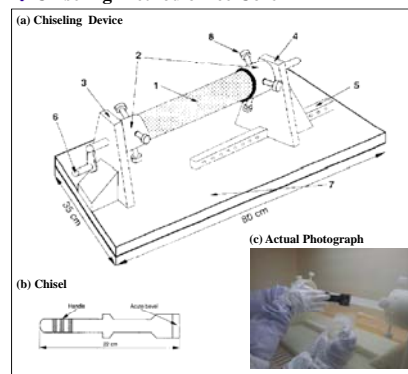


Figure 3. Schematic diagram of (a) the decontamination system, (b) stainless steel chisel used for the chiseling (Candole et al., 1994) and (c) actual photograph of decontamination process by chiseling.

3. Results and Discussion

Data Accuracy

Table 2. Concentration of CRM in SLRSS solution (10 times sample) and melting system procedural blank.

Element	IDL	MSPDL	MSPB	Measured	Certified	RE(%)
⁹⁰ Rb	0.030	0.055	<IDL	1282.7	1300 ^a	-1.3
⁸⁷ Se	0.114	0.117	0.340±0.235	57591.1	53600±1300	-7.4
¹⁰⁰ Mo	0.041	0.082	0.527±0.082	224.7	270±40	16.8
¹¹⁴ Cd	0.028	0.015	0.096±0.030	9.1	6±1.4	-52.3
¹²⁵ Sb	0.028	0.005	0.240±0.005	275.1	300	14.3
¹³⁷ Ba	0.127	0.369	0.208±0.739	15602.0	14000±500	-11.4
²⁰¹ Tl	0.021	0.039	<IDL	4.3	4 ^a	-8.3
²⁰⁹ Pb	0.064	0.497	0.935±0.995	75.7	81±6	6.6
²¹⁰ Pb	0.129	0.102	<IDL	15.0	13±14 ^a	-10.8
²¹⁰ Pb	0.018	0.125	<IDL	92.3	93±6	0.8
²¹⁴ Pb	0.087	0.142	<IDL	404.2	317±33	27.5
²³² Cr	0.824	0.402	1.139±0.805	239.9	208±23	-15.4
²³⁸ Mn	0.250	0.218	1.467±0.435	4433.4	4330±180	-2.4
²⁴⁰ Fe	4.673	65.629	152.511±131.257	92980.0	91200±5800	-2.0
²⁴⁰ Co	0.075	0.256	0.383±0.512	57.4	50	-14.8
²⁴⁰ Cu	0.660	26.515	38.808±53.029	18954.7	17400±1300	-8.9
²⁶⁴ Zn	1.718	3.704	7.791±7.408	964.8	845±95	-14.2

Note: ^a unit: ng/L, ^b reference values of reported in "Geochem" website; IDL (instrumental detection limits, 3σ of 12 times measurement); MSPB (Melting system procedural blank), MSPDL (Melting system procedural detection limits, 3σ of 6 times of measurement); RE (Relative errors)

Decontamination Efficiency

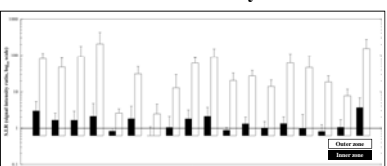


Figure 4. Decontamination efficiencies of trace elements by the melting system. The efficiency was evaluated by the ratios of instrumental intensities between system blank and artificial ice core.

Inter-comparisons of Chiseling Method and Melting System

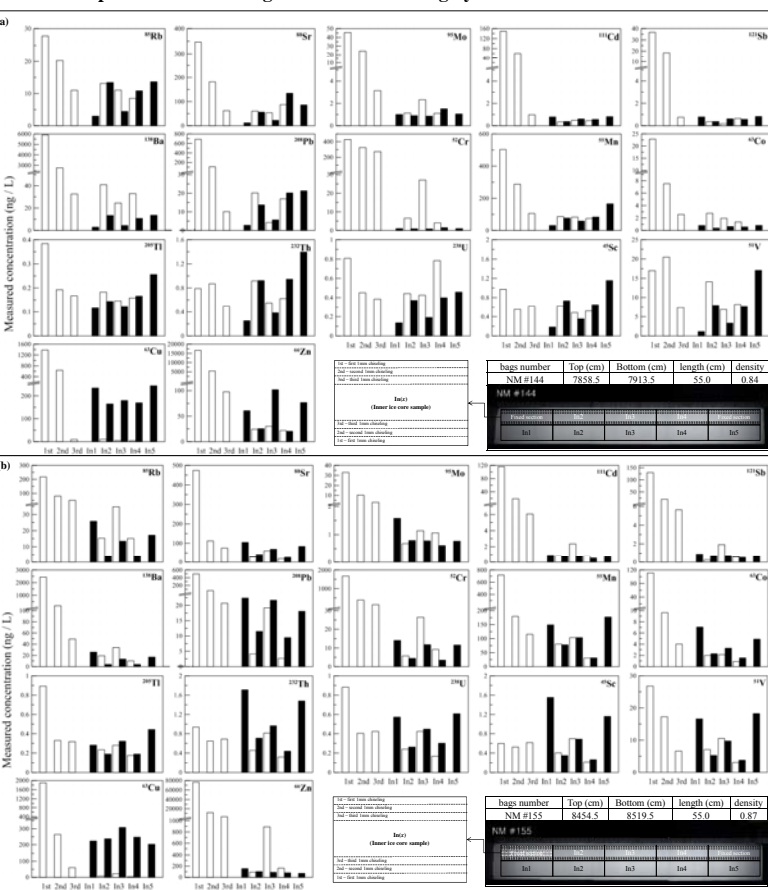


Figure 6. Inter-comparisons of the trace elements concentrations of NEEF firm core samples treated by chiseling (white bar) and melting (black bar). (a) 78.585 ~ 79.135 m; (b) 84.545 ~ 85.195 m

Application for NEEF firm core



The North Greenland Eemian Ice Drilling "NEEF" is an international ice core research project aimed at retrieving an ice core from North-West Greenland (camp position 77.45°N 51.06°W) reaching back through the previous interglacial, the Eemian.

Elements	Min.	Max.	Avg.	Ref. ¹	Ref. ²	Ref. ³	Ref. ⁴	Ref. ⁵
⁹⁰ Rb	3.8	48.4	13.0	3.7				
⁸⁷ Se	6.0	131.6	60.2	6.7				120
¹⁰⁰ Mo	0.5	2.6	1.3					
¹¹⁴ Cd	0.4	21.1	2.4	0.3	0.7	0.771		0.2
¹²⁵ Sb	1.2	6.2	3.1					
¹³⁷ Ba	0.12	4.2	1.3	0.5				
¹³⁷ Ba	8.6	174.9	57.9					93.1
²⁰¹ Tl	0.08	58.7	28.5	7.6	4.3	10.2	up to 50	0.5
²⁰⁹ Pb	0.48	3.6	1.3					0.1
²¹⁰ Pb	0.13	4.3	1.3					0.2
²¹⁰ Pb	0.04	1.8	0.5	0.01				0.0
²¹⁴ Pb	0.18	1.2	0.5	0.06				0.9
²¹⁴ Pb	0.19	17.5	6.1	6.7				0.2
²³² Cr	2.1	26.2	9.4	44.0				3.4
²³⁸ Mn	11.9	575.8	130.8	10.0				211
²⁴⁰ Fe	42.5	6086.2	2377.1	2900.0				1250
²⁴⁰ Co	0.12	102.5	7.3	2.7				0.6
²⁴⁰ Cu	13.5	240.2	93.8	2.8	8.0			2.0
²⁶⁴ Zn	51.6	1499.3	373.3	164.0	103.0			200
²⁷¹ Al	299.5	6224.4	2028.7	4300.0				200
²⁷¹ Al	0.91	25.6	9.4					

Note: This study (NEEF, Greenland, 1776-1884AD when formal age applied)
 Ref.¹ Candole et al., 1994 (Summit, central Greenland, 1773AD)
 Ref.² Kröhler et al., 2005 (Canadian High Arctic, minimum value since 1845AD)
 Ref.³ McConnell and Edwards, 2006 (ACT2, Greenland, annual average during 1772-1860AD)
 Ref.⁴ McConnell et al., 2002 (Summit, Greenland, 1750-1800AD, deduced from Figure 1)
 Ref.⁵ Choe et al., 2006 (min values of compiled Greenland ice concentrations since 1491 BP)

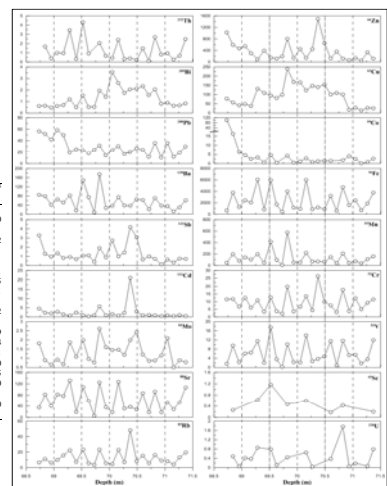


Figure 5. The concentrations of trace elements in the NEEF firm core (68.675 ~ 71.425 m).

4. References

- Candole et al., 1994, *Anal Chim Acta* **29**: 9-16
- Hong et al., 2000, *Kor J Pol Res* **11**: 35-47
- Kaufmann et al., 2008, *Environ Sci Technol* **42**: 8044-8050
- Bigler et al., 2011, *Environ Sci Technol* **45**: 4483-4489
- McConnell et al., 2002, *Environ Sci Technol* **36**: 7-11
- Osterberg et al., 2006, *Environ Sci Technol* **40**: 3355-3361
- KOPRI, 2010, Korea Polar Research Institute PK09050 **32p** (in Korean)
- Hong et al., 2014, Development of advanced melting system for measurement of trace elements and ions in ice core. *J Glaciol* (Submitted)