

Instruments and Methods

A technique for continuous detection of drill liquid in ice cores

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ABSTRACT. When drilling ice cores deeper than ~100 m, drill liquid is required to maintain ice-core quality and to limit borehole closure. Due to high-pressure air bubbles in the ice, the ice core can crack during drilling and core retrieval, typically at 600–1200 m depth in Greenland. Ice from this 'brittle zone' can be contaminated by drill liquid as it seeps through cracks into the core. Continuous flow analysis (CFA) systems are routinely used to analyse ice for chemical impurities, so the detection of drill liquid is important for validating accurate measurements and avoiding potential instrument damage. An optical detector was constructed to identify drill liquid in CFA tubing by ultraviolet absorption spectroscopy at a wavelength of 290 nm. The set-up was successfully field-tested in the frame of the NEEM ice-core drilling project in Greenland. A total of 27 cases of drill liquid contamination were identified during the analysis of 175 m of brittle zone ice. The analyses most strongly affected by drill liquid contamination include insoluble dust particles, electrolytic conductivity, ammonium, hydrogen peroxide and sulphate. This method may also be applied to other types of drill liquid used at other drill sites.

INTRODUCTION

The ice sheets of Antarctica and Greenland offer long and continuous climate records. Ice cores have been successfully drilled to the bedrock in central Greenland (2.5–3.1 km depth) and Antarctica (2.8–3.7 km depth) (Bentley and Koci, 2007) with the development of advanced ice-core drilling and recovery technology (Johnsen and others, 2007; Orombelli and others, 2010). When drilling ice cores deeper than ~100 m depth, drill liquid is required to prevent borehole deformation (Talalay and Hooke, 2007) and to ensure high-quality ice-core retrieval (Johnsen and others, 2007). Different types of drill liquid have been used for deep ice-core drilling (Talalay and Gundestrup, 2002); for example, at the Dye-3 drilling site in south Greenland (Gundestrup and Hansen, 1984) a combination of Jet A-1 fuel and perchloroethylene was used (Gundestrup and others, 1984). Ethanol–water solutions have been used as a hydrophobic drilling liquid in Arctic and Antarctic glaciers (Zagorodnov and others, 1994). At the North Greenland Ice Core Project (NorthGRIP) site (NorthGRIP members, 2004), ExxsolD-60 solvent was used with hydrochlorofluorocarbon 141b (HCFC-141b) as a densifier (Steffensen, 2011).

The drill liquid must meet a few essential criteria: the freezing point should be much lower than that of ice at the drill site, the density should be identical to that of ice, and it must be reasonably viscous as it also acts as a drill lubricant and a medium for ice-chip transport. Ideally, it should also be environmentally non-hazardous and safe to humans. At the North Greenland Eemian Ice Drilling (NEEM) (77°45' N, 51°09' E; 2480 m a.s.l.; www.neem.dk) site (Table 1) the drill liquid used was a mixture by volume of two to three parts Estisol240 coconut oil extract and one part Coasolester mixture (both Dow Haltermann, Germany).

Below the firn column close-off depth, trapped gases are present in the ice in the form of bubbles. At depths of ~1200 m, high pressures transform the air bubbles into

clathrates (Kipfstuhl and others, 2001). In the 600–1200 m depth interval the ice becomes brittle as the internal pressure in the air bubbles exceeds the tensile strength of the ice crystal structure. When ice from this brittle zone is brought to the surface, the pressure in the air bubbles in the ice greatly exceeds the atmospheric pressure, so pressure-driven volume expansion has the potential to crack the ice (Uchida and others, 1994). Through these cracks drill liquid can seep into the core and contaminate the inner section of the ice core.

Problems with drill liquid contamination were also observed for the bottom section of the NorthGRIP ice core. The basal ice was close to pressure-melting point in the borehole, which made drilling difficult and the ice brittle when brought to the surface. The warm ice can have liquid water between the crystals, and as the ice core is transported through the cold central part of the ice sheet the expansion due to freezing of this liquid water can make the core brittle. Therefore, many core breaks occurred during drilling and subsequent core handling (Svensson and others, 2011). When NorthGRIP deep ice was analysed by the continuous flow analysis (CFA) system (Bigler and others, 2011), many of the insoluble dust data were compromised due to drill liquid contamination (Svensson and others, 2011).

To avoid contamination in the CFA, the ice sample is cut with a typical cross section of 35 mm × 35 mm and a length of 0.55–1.10 m. Both ends of the ice stick are carefully cleaned with a microtome knife before analysis. Breaks or fractures within the section are removed. For the CFA of the NEEM brittle ice, only non-fractured ice-core sections with a minimum length of 10 cm were analysed, with several metres of brittle ice found to be unsuitable for the CFA. When the ice sample is to be melted, it is placed on a melt-head that separates the outer part of the sample from the inner part. Meltwater from the outer part of the melt-head is pumped away more quickly than that of the inner part, further ensuring that there is no mixing between the inner

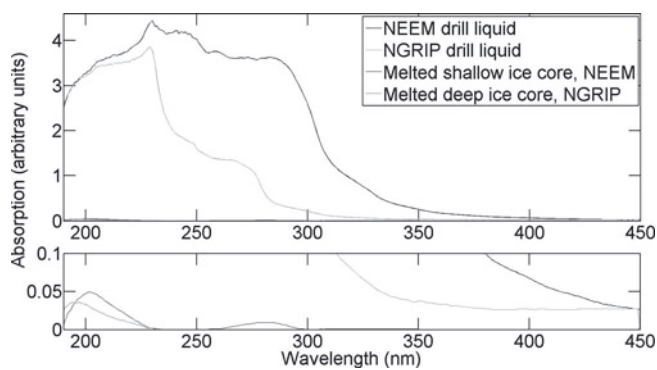


Fig. 1. UV absorption spectra for drill liquid used at the NorthGRIP and NEEM sites and for melted ice-core samples. The bottom graph shows a zoom of the lowest absorption values.

and outer sections of the CFA sample. Only the inner part of the sample is used for the CFA (Bigler and others, 2011). Drill liquid can only enter the analytical instrumentation of the CFA system by being present in the inner section of the CFA stick prior to melting. This can occur if the drill liquid seeps through small cracks in the ice or if the drill liquid is refrozen and trapped into the ice matrix.

Drill liquid may interfere with analytical instruments by various means. Many CFA detection systems take advantage of the different optical properties between water and the molecule to be determined. The different optical properties of drill liquid may lead to false results. Fluorescence measurements can also be enhanced or altered by the presence of detergents in the sample (Traversi and others, 2007). Furthermore, the viscous properties of drill liquid may result in its sticking to the inner walls of the CFA tubing and fittings, creating variations in the tubing diameter and altering liquid flow rates through the CFA system. This can interfere with the flow of the sample, and may clog components where the sample flow is restricted (e.g. filters or reaction columns). In this work, we present a non-intrusive method for continuous detection of drill liquid in a CFA system based on ultraviolet (UV) spectroscopy and apply this to the brittle zone section of the NEEM ice core.

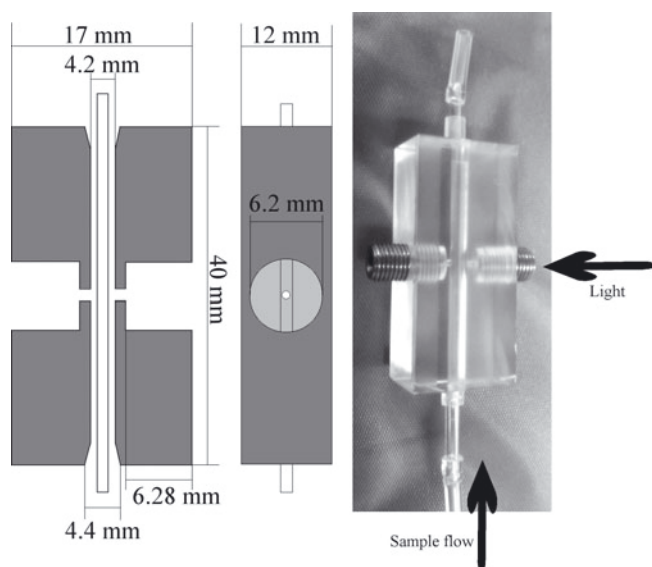


Fig. 2. Schematic of the drill liquid detection flow cell used at NEEM. The flow cell consists of a quartz tube mounted in a plastic frame.

Table 1. Properties of the NEEM drill liquid components (Larsen and others, 2012)

	Coasol [®]	Estisol [®] 240
Manufacturer	DOW	DOW
Melting point	<−60°C	<−50°C
Boiling point	274–289°C	255–290°C
Flash point	131°C	136°C
Explosive limit	0.6–4.7% (vol.)	None
Vapour pressure (20°C)	0.004 kPa	N/A
Density (20°C)	960 kg m ^{−3}	863 kg m ^{−3}
Density (−30°C)	995 kg m ^{−3}	898 kg m ^{−3}
Viscosity (20°C)	0.053 m ² s ^{−1}	0.03 m ² s ^{−1}
Viscosity (−30°C)	0.25 m ² s ^{−1}	0.13 m ² s ^{−1}
Auto-ignition temperature	400°C	None
Biodegradable	Yes	Yes
Special protection	No	No
Hazardous material	No	No
Explosive risk	None	None
Max. workplace air levels	None	None

METHODS

Drill liquid absorption spectra

A Genesys 10UV Spectrophotometer (Thermo Scientific, USA) was used to determine the light absorption spectra of drill liquid from NorthGRIP (D-60/HCFC-141b) and NEEM (Estisol240/Coasol). Samples were analysed in QS1000 quartz cuvettes (Hellma Analytics, Mullheim, Germany) at wavelengths in the 190–1100 nm range. To calibrate the system and determine a baseline of relative absorption, ultrapure water (Millipore Advantage, $\geq 18.2 \text{ M}\Omega \text{ cm}^{-1}$, Millipore Corp.) was used. Both the NorthGRIP and NEEM drill liquids were found to have strong absorption in the UV range, >50 times greater than the firn and ice-core sample. The set-up was also tested on samples from a NEEM shallow firn core (~10 m depth) and on NorthGRIP deep ice (~2706 m depth) (Fig. 1).

Instrument and set-up

The flow cell (Fig. 2) consists of a hand-blown quartz glass tube held in a plastic frame by silicone tubing. A broadband deuterium halogen light source (DT-Mini-2-GS, Ocean Optics, USA) was mounted perpendicular to the quartz tube using an optical fibre, with the other end of the optical path connected to a USB2000 UV-VIS spectrometer (Ocean Optics, USA). The program OOIBase32 (Ocean Optics, USA) was set to monitor at $\lambda = 290.00 \text{ nm}$, which was found to be the optimal wavelength for UV absorption delivered by the light source. The flow cell was mounted so the water flow was directed vertically upwards to avoid the possibility of trapping air bubbles in the optical path.

Signal interference and identification

Air bubbles can interfere with the detection of drill liquid as they also absorb light in the UV range and hence produce a similar signal to that of drill liquid. For this reason a second wavelength of $\lambda = 435.83 \text{ nm}$ was also monitored in order to discriminate air bubbles from drill liquid. A MATLAB script was written to automatically distinguish drill liquid from air bubble signals (Fig. 3a and b).

In most cases the presence of drill liquid was unambiguously detected. In a few exceptional cases, however, the drill

liquid did not behave as expected. In some cases, the 290 nm wavelength was only partially absorbed and the 435.83 nm wavelength displayed minimal absorption (Fig. 3c and d). The possible presence of other contaminants was investigated to explain this behaviour, such as the CFA melt-head cleaning agent Isopropanol ($(\text{CH}_3)_2\text{CHOH}$); however, Isopropanol did not absorb light at the monitored wavelengths. This behaviour was attributed to the presence of a very small droplet of drill liquid (Fig. 3c) or a sticking droplet that is elongated through contact with the tubing walls (Fig. 3d).

These exceptional cases were later confirmed to be due to the presence of drill liquid, because contamination spikes were also determined in the NEEM CFA.

FIELD MEASUREMENTS

In the summer of 2011 the detector was used at the NEEM ice-core drilling site, where brittle zone ice (depths 608.85–1280.95 m) was analysed using the Bern CFA system (Kaufmann and others, 2008). At the beginning and end of the brittle zone (608.85 m and 1280.95 m depths) the ice was of good quality with no cracks, whereas the middle of the brittle zone exhibited very poor ice-core quality. Between 860 and 1129 m depth, only 7 m of ice was of suitable quality for CFA. The drill liquid detector was connected in parallel to the other CFA detectors. A total of 158 runs of ~ 1.1 m long ice-core samples were analysed, and drill liquid was detected in 27 instances. Of these 27 cases of contamination, only 9 were in the ice-core sample. The instances of drill liquid determined within ice-core sections were at depths of 644–648, 1248–1249, 1269–1272 and 1280–1281 m. The majority of drill liquid contamination events occurred either before or after the ice-core measurement, although drill liquid still entered the CFA system and interfered with the instrumentation. When the CFA data were processed, contamination spikes were identified by comparing them with the drill liquid detection channel response.

Drill liquid interferences and CFA data

The CFA systems primarily work by absorption or fluorimetric detection, although some analytes are determined by dedicated commercial instruments, such as meltwater electrolytic conductivity (conductivity) (Amberscience 3082 with micro-flowcell, USA) and insoluble dust particle (dust) (Klotz Abakus, Germany).

When ice is melted, the meltwater is split into different channels, each leading to a detector or flow cell. Absorption detection usually works by mixing the sample with a reagent, adding a buffer to stabilize the mixture and then passing it through an illuminated flow cell. The amount of light absorbed is then converted into a molar mass or concentration by calibration to standard solutions of known concentration.

In fluorimetric detection the sample is mixed with a reagent and buffer and excited by light at one wavelength, resulting in fluorescence (light emission) at another wavelength. The intensity of the emitted light is converted into a molar mass or concentration in a similar way to absorption measurements.

Some analytical systems make use of columns to eliminate interferences and/or to increase the sensitivity of the technique. To avoid interferences by multivalent cations (e.g. magnesium and calcium) in the determination of

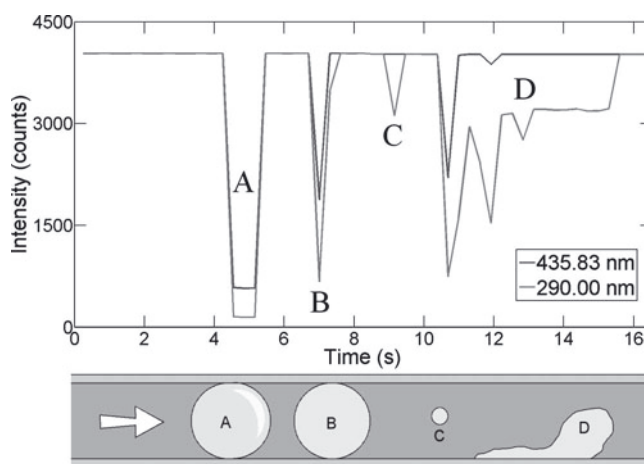


Fig. 3. By monitoring two wavelengths, drill liquid ($\lambda = 290.00$ nm) and air bubbles ($\lambda = 435.83$ nm) can be distinguished. Signal A, with a $\lambda = 435.83$ nm intensity lower than 1500 counts, is an air bubble; signal B is a typical example of NEEM drill liquid detection; signal C is NEEM drill liquid in the form of droplets; and signal D is an example of a drop of NEEM drill liquid that is in contact with the side of the quartz tubing.

sulphate, a cation exchange column is used. For the determination of sodium an immobilized enzyme reactor (IMER), a column of enzymes coated on glass beads, is required (Bigler and others, 2007). Such columns may become clogged by drill liquid, thus introducing sample artefacts, biases or complete failure of the analytical system.

The CFA detection channels are differently affected by the presence of drill liquid:

Conductivity. The electric conductivity cell measures the free ions, through a flow cell with two electrodes (Bigler and others, 2011). The conductivity was observed to decrease when drill liquid passed through the detection cell.

Dust. The dust detector measures the attenuation of laser light through an aperture caused by shadowing of the particles in the liquid stream. The drill liquid droplets strongly absorb light, so the dust counts become artificially high. This behaviour was also observed for the deepest NorthGRIP ice (Svensson and others, 2011).

Ammonium is detected by fluorescence, where the sample is excited by light at a wavelength $\lambda = 365$ nm, and fluoresces at $\lambda = 420$ nm (Kaufmann and others, 2008). The presence of drill liquid results in erroneously high concentrations.

Hydrogen peroxide is detected by fluorescence, where the sample is exposed to light of wavelength $\lambda = 340$ nm and fluoresces at $\lambda = 400$ nm (Kaufmann and others, 2008). The presence of drill liquid results in erroneously high concentration.

Sulphate. Only two of the 27 cases of drill liquid contamination produced an interference in the sodium signal, which indicated an erroneously high concentration. The sulphate detector works on absorption at $\lambda = 660$ nm (Kaufmann and others, 2008), which is beyond the absorption range of the drill liquid. The effect of the drill liquid might be to reduce the efficiency of the cation exchange column (Röthlisberger and others,

2000) which removes interfering multivalent cations from the sample stream.

CONCLUSIONS AND FURTHER DEVELOPMENT

A simple and robust system has been developed that continuously detects and identifies any presence of drill liquid contamination in an ice-core CFA system. The set-up was applied at the NEEM ice-core drilling site where it successfully monitored the CFA liquid stream throughout the brittle ice zone measurement campaign. The system also has potential to detect other types of drill liquid in other cores, such as used at NorthGRIP.

Potentially, the system can be improved by the use of powerful LEDs emitting at 240 nm wavelength with better stability and reliability, and a longer lifetime than the deuterium halogen light source used here. If applied, it would have to be in conjunction with another LED so the air bubbles could also be detected.

A possible development of the CFA system would be to remove the drill liquid from the analytical system before it reaches any sensitive instruments. Such a system could operate either passively (in a detection-warning mode) or actively to ensure that drill liquid does not enter the analytical system. A valve could switch at the presence of drill liquid and divert contaminated meltwater away from the CFA instruments. The loss of sample resulting from such a mechanism must be balanced against the cost of time, instruments and spare parts required to deal with instrument failures resulting from the introduction of drill liquid.

A more passive system could be used to identify and quantify the amount of drill liquid present in the samples. Such a system could be used in cases where drill fluid coats the inside of the tubing without directly influencing some detectors, and it would provide the CFA operator with an additional indication of when a full-system maintenance and cleaning is needed.

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