The Frozen Diary – history unlocked with the help of ultrapure water

WEATHER MONITORING

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For more than ten years Carlo Barbante and his research team at the University of Venice's Department of Environmental Sciences have been digging up the Antarctic snow to look for trace levels of heavy metals. The snow is a deep-frozen record of atmospheres of centuries past, and the heavy metals show how atmospheric pollution has changed with the passing years.

Professor Carlo Barbante of the University of Venice is interested in atmospheric pollution and, in particular, how it has changed over the years. As snow falls it washes pollutants like heavy metals from the atmosphere and the Antarctic snow – frozen for centuries – provides a historical record of atmospheres past. The levels of heavy metals such as cadmium, lead, zinc and copper in these frozen records are very low, varying from thousands of picograms per gram (pg/g) for present day Greenland surface snow to tenths of a pg/g for Antarctic snow from the Holocene epoch (up to about 50,000 years ago), so the purity of the samples is of critical importance. On a recent expedition the team visited Coats Land, Antarctica, to take samples covering a period of about seventy years from about 1915 to about 1985. This is the story of that expedition.

Sampling

Sampling the Antarctic snow involved digging an 8.3m deep sampling pit from which potentially contaminating metal objects were carefully excluded – including the removal of operators' jewellery and even spectacles[1]. The operators, who did all the digging and sampling with acid-cleaned stainless steel tools, wore clean room clothing whilst they were cutting sample blocks about 40cm x 30cm x 33cm from one wall of the pit, each representing about two years of history. They scraped the sample blocks with an acid-cleaned polyethylene scraper to remove any metallic contamination, and then stored them in acid-washed double polyethylene bags in a cold storage pit. When all the samples had been taken they were collected by ship and transported to the laboratories in the ship's cold store, so that the temperature was maintained below 10°C at all times.

In the laboratory, the blocks were sub-sampled, using protocols designed to give as representative samples as possible, in a specially designed laminar flow clean bench inside a cold room kept at 15°C. The clean bench and most of the handling equipment was constructed from polyethylene and acid cleaned before use. The sub-samples were placed in polyethylene bottles, acidified with nitric acid and then re-frozen for storage until analysis.

Sample Preparation and Analysis

In trace analysis two factors are of fundamental importance: protection of the sample from contamination and accuracy of the measurement and the University of Venice has special clean room facilities with minimum metallic content. Even the HEPA filters and air fans are constructed from low density polyethylene.

Earlier work[2] had already given the researchers confidence that Sector Field ICP-MS could be used to analyse the samples with sufficient repeatability, provided that the samples were thirty times concentrated by sub-boiling evaporation. The sample concentration stage clearly concentrates any earlier contamination of the sample, and is itself another potential source of contamination. For this reason, the researchers were keen to find a technique that would allow the samples to be analysed directly without any pre-concentration step.

They chose a ThermoFinnigan inductively coupled plasma sector field mass spectrometer (ICP-SFMS) with an ESI (Elemental Scientific) PFA-100 microflow nebuliser connected to a polyfluoroacetate double pass spray chamber maintained at room temperature. The thawed sample was drawn from the bottle via a PFA capillary, using a Spetec peristaltic pump fitted with a Tygon tube. The system was pre-cleaned, to minimise the possibility of contamination, by passing ultrapure nitric acid (1% solution in ultrapure water) for at least twenty hours before attempting any measurements. As an indicator they used lead 208Pb and considered the instrument clean when this stabilised at less than 400 counts per second.

The accuracy of instruments like the ICP-SFMS is dependent on the purity of the blanks and standards used for calibration, and the double distilled nitric acid used for cleaning the introduction system and acidifying the samples had a typical lead content of 0.13pg/g. Each day the tuning parameters of the ICP-SFMS were optimised against a 1.0ng/g solution of indium acidified with the ultrapure nitric acid so as to obtain the maximum signal response and stability. Calibration of the ICP-SFMS was against a 100µg/g multi-element standard solution supplied by Merck, which was diluted with the same ultrapure water as was used for blanks.
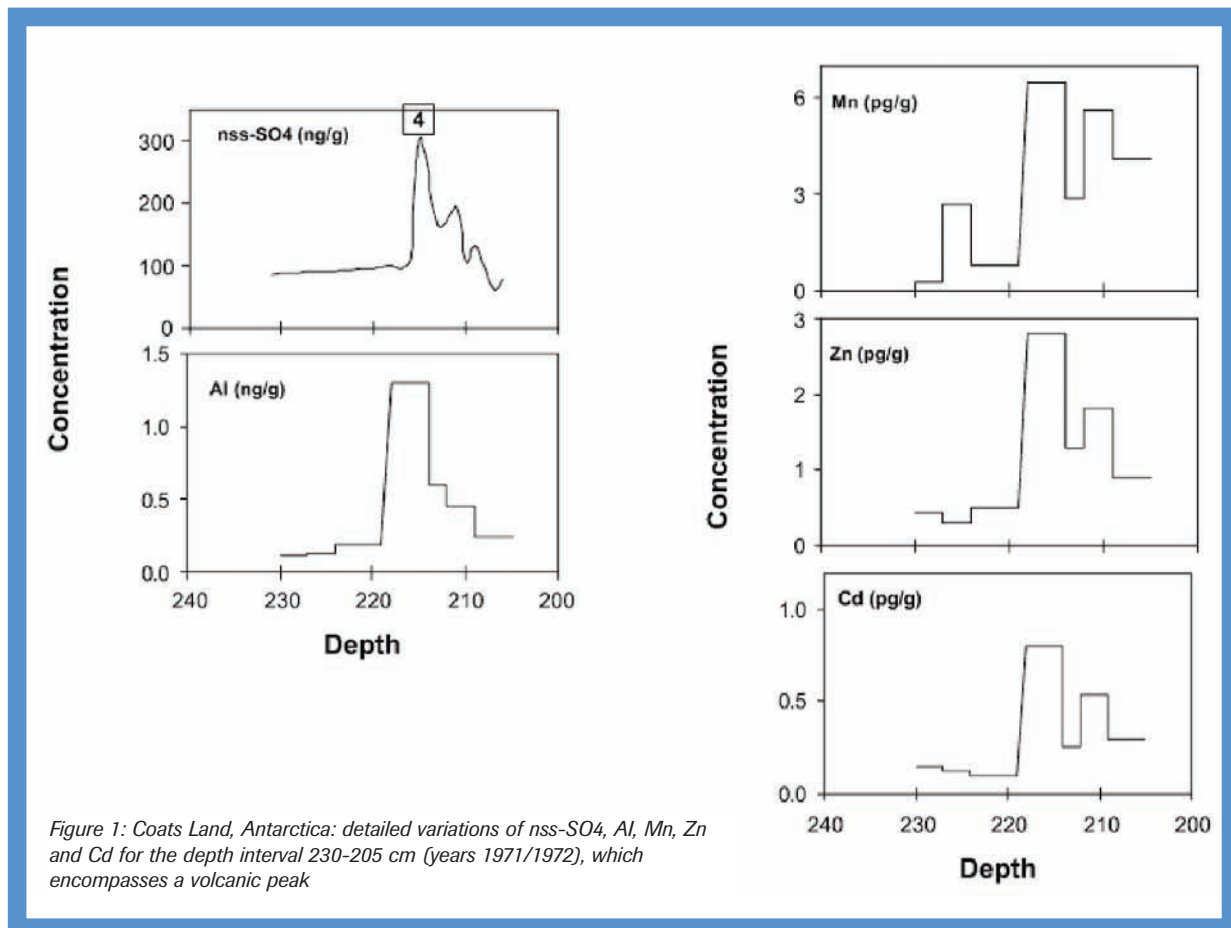
Ultrapure Water

Giulio Cozzi is the University of Venice's ultrapure water specialist, and he is meticulous in his attention to detail. For his

most recent spectrometry work, he chose an ELGA LabWater PURELAB Ultra Analytic.

The PURELAB Ultra Analytic is designed for "polishing" pre-treated water. In the University of Venice's laboratory, it is fed with water that has been pre-treated by reverse osmosis and has a resistivity better than 0.1MΩ.cm. The water is fed through a primary purification cartridge, which combines mixed bed ion exchange resins and an organic adsorbent to remove both ionic and organic impurities. It is then exposed to ultraviolet irradiation using a low pressure mercury lamp, which generates UV at wavelengths of 185nm and 254nm. The longer wavelength radiation has a powerful bactericidal effect, whilst the shorter wavelength generates free hydroxyl radicals which photo-oxidise residual trace levels of organic matter to form charged species. The second purification cartridge removes the ions generated by photo-oxidation as well as any other trace residual ions, which remain after the primary cartridge, principally those such as sodium which are present at relatively high levels in the feed water. Resistivity monitoring between the two cartridges ensures that exhaustion of the primary cartridge is detected whilst most of the polishing capacity still remains in the secondary cartridge, so that there is no possibility of the treated water quality deteriorating. The water from the secondary cartridge is filtered to 0.05µm by a membrane microfilter and is then recirculated to the primary purification cartridge until required for use.

Maintaining water quality is vital to successful operation and this is confirmed by resistivity monitoring after each

Figure 1: Coats Land, Antarctica: detailed variations of nss-SO4, Al, Mn, Zn and Cd for the depth interval 230-205 cm (years 1971/1972), which encompasses a volcanic peak

purification stage and in-line real time measurement of total organic carbon (TOC).

Water Purification Performance

Whilst the resistivity of the ultrapure water provides an easily measurable indication that the water purification system was working well, it was important for Giulio Cozzi's team to know exactly what contaminants were present in the ultrapure water on a day-to-day basis. Consequently whenever analyses of snow samples were carried out, the team also carried out an analysis of the ultrapure water. A typical set of results[3] (for week commencing 24 March 2003) is given in Table 1.

TABLE 1 – Trace Element Analysis of Water from Ultra Analytic

Element		Units	Value
Aluminium	Al	pg/g	2.9
Antimony	Sb	pg/g	3.2
Arsenic	As	pg/g	4.7
Barium	Ba	pg/g	< 2.3
Beryllium	Be	pg/g	0.04
Bismuth	Bi	pg/g	< 0.6
Cadmium	Cd	pg/g	0.16
Chromium	Cr	pg/g	2.0
Cobalt	Co	pg/g	2.0
Copper	Cu	pg/g	4.0
Iridium	Ir	pg/g	0.002
Iron	Fe	pg/g	2.3
Lead	Pb	pg/g	0.7
Manganese	Mn	pg/g	1.1
Mercury	Hg	pg/g	1.3
Molybdenum	Mo	pg/g	2.0
Nickel	Ni	pg/g	4.2
Platinum	Pt	pg/g	0.001
Selenium	Se	pg/g	1.0
Silver	Ag	pg/g	0.18
Uranium	U	pg/g	0.005
Vanadium	V	pg/g	0.25
Zinc	Zn	pg/g	2.2

The impurity concentrations in the samples can approach the purity levels of the blanks, so it is essential that these low levels can be maintained with confidence.

Results

Significantly higher levels of heavy metals were found in the samples taken from the outermost two centimetres of the

blocks compared with those from the interior, indicating surface contamination, and showing just how difficult it is to obtain completely uncontaminated environmental samples. For this reason only samples from the centres of the blocks were analysed.

The variations in concentrations between samples from different depths have helped researchers to understand patterns of heavy metal inputs into Antarctica. These are generally considered to be associated with the long range transport of crustal dust from the arid areas of South America, South Africa and Australia. Additional inputs can also occur as a result of major environmental events such as fallout from volcanic eruptions. An example is shown in figure 1, where the effect of a volcanic eruption in 1971/2 can be seen in the raised levels of non-sea-salt sulphate and various metals.

The work carried out at the University of Venice has demonstrated that, by using ultraclean sampling procedures and sample preparation protocols together with a source of consistent ultrapure water it is possible to determine trace levels of heavy metals without a pre-concentration step. ELGA LabWater, the laboratory water specialist division of VEOLIA WATER, are pleased to assist European research at the cutting edge of trace element analysis by providing that ultrapure water.

REFERENCES

1 Planchon F A M et al "Ultrasensitive Determination of Heavy Metals at The Sub-Picogram Per Gram Level in Ultraclean Antarctic Snow", Analytica Chimica Acta 450 (2001) 193 205

2 Barbante C et al "Direct Determination of Heavy Metals at Picogram per Gram Levels in Greenland and Antarctic Snow" J Anal At Spectrom, 1999 12 (1997) 925 – 931

3 Private communication with Dr G Cozzi, University of Venice, April 2003