

AMS AND MICROPROBE ANALYSIS OF COMBUSTED PARTICLES IN ICE AND SNOW

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ABSTRACT. Ice cores and snow pits of the cryosphere contain particles that detail the history of past atmospheric air compositions. Some of these particles result from combustion processes and have undergone long-range transport to arrive in the Arctic. Recent research has focused on the separation of particulate matter from ice and snow, as well as the subsequent analysis of the separated particles for ^{14}C with accelerator mass spectrometry (AMS) and for individual particle compositions with laser microprobe mass analysis (LAMMA). The very low particulate concentrations in Arctic samples make these measurements a challenge. The first task is to separate the particles from the ice core. Two major options exist to accomplish this separation. One option is to melt the ice and then filter the meltwater. A second option is to sublime the ice core directly, depositing the particles onto a surface. This work demonstrates that greater control is obtained through sublimation. A suite of analytical methods has been used for the measurement of the carbon in snow and ice. Total carbon was analyzed with a carbon/nitrogen/hydrogen (CHN) analyzer. AMS was used for the determination of carbon isotopes. Since source identification of the carbonaceous particles is of primary importance here, the use of LAMMA was incorporated to link individual particle molecular-structural patterns to the same group of particles that were measured by the other techniques. Prior to this study, neither AMS nor LAMMA had been applied to particles contained in snow. This paper discusses the development and limitations of the methodology required to make these measurements.

INTRODUCTION

Since the industrial revolution, the concentrations of anthropogenically produced atmospheric constituents have risen dramatically to the point where industrial and motor vehicle emissions, and residential activities such as wood burning, now dominate the natural biogeochemical cycling in many urban, and to some extent, rural and remote environments. Many of the anthropogenically produced materials introduced into the atmosphere, like polycyclic aromatic hydrocarbons (PAHs) and their derivatives, are of great interest due to their toxic and carcinogenic properties (Sarma 1995). The impact of atmospheric pollution is most readily perceived by visibility degradation (Pilinis and Pandis 1995). Carbonaceous aerosols are major contributors to light absorption. Changes in light scattering and light absorption affect Earth's albedo and are directly correlated to global stratospheric temperature changes (McElroy 1994). Most important, anthropogenic emissions into the atmosphere must be delineated from natural components and the sources of these anthropogenic components must be determined. Reliable scientific data on anthropogenic emissions are crucial for the institution of applicable policies and establishing reasonable control strategies of man-made emissions.

Investigations of total carbon and elemental concentrations in Arctic snow and ice have been performed in the past. Chýlek *et al.* (1987) surveyed snow samples for aerosol and graphitic carbon content from southern New Mexico, west Texas, Antarctica and Greenland. Black carbon concentrations were determined for ice core samples from the Greenland Dye-3 core covering the time period 3380–100 BP (Chýlek, Johnson and Wu 1992). Black carbon concentrations were also determined from the Greenland Ice Core Project 2 (GISP2) core (Chýlek *et al.* 1995). Cachier and Pertuisot (1994) reported values for particulate carbon in Arctic ice. Peters *et al.* (1995) determined the

depositional trend of polycyclic aromatic hydrocarbons (PAH) and elemental carbon to the Agassiz Ice Cap, Ellesmere Island, Canada. Carbon dioxide trapped in ice cores has also been used to date ice cores *via* AMS (Wilson and Donahue 1990; Wilson 1995).

We discuss here the application of accelerator mass spectrometry (AMS) and laser microprobe mass analysis (LAMMA) to the analysis of carbonaceous particles in snow and ice. These measurements are targeted to obtaining source information from the samples. Specific application of these techniques to carbonaceous particles in snow and ice has not been performed before. These methods are first tested on snow from an urban environment where carbon concentrations are higher. LAMMA is also applied to snow collected at Summit, Greenland.

METHODS

Particle Separation from Snow

The AMS and LAMMA analysis techniques do not accept aqueous samples, so particles must be separated from the snow or ice samples. Techniques for particle separation include filtration, sublimation and evaporation, among others.

Filtration is the predominant method used for separation of particles from snow and ice (Chýlek *et al.* 1987; Chýlek, Johnson and Wu 1992; Cachier and Pertuisot 1994; Chýlek *et al.* 1995). The procedure is simple and large samples may be filtered quickly. For carbon analysis, quartz filters are normally chosen due to their low carbon content. Quartz filters may also be heated to high temperatures (above 900°C) to remove any carbon contamination. The biggest disadvantage to particle filtration is the particle collection efficiency. Although the filters are better than 99% efficient in trapping particle sizes of interest, some particles adhere to the filtration apparatus and are not deposited on the filter. Chýlek *et al.* (1987) achieve particle collection efficiencies of 66–85% for aluminum oxide particles on quartz filters. These filtration efficiencies are consistent with results obtained when urban dust (both SRM 1648 and 1649) was mixed with crushed ice, melted, and then filtered through quartz filters. Although the filtration efficiency was less than desirable, the reproducibility of the filtration efficiency proved to be even less satisfactory. For filtration, snow and ice samples must be melted. This may cause a problem because prolonged time (greater than a few hours) at elevated temperatures allows biological growth in the sample (Chýlek *et al.* 1987). To decrease melting times, both microwaves (Chýlek, Johnson and Wu 1992) and external heat sources (Cachier and Pertuisot 1994) have been used. While this may reduce sample melting times, the microwave or elevated temperatures may affect sample chemistry. Other negative aspects of filtration include the possible addition of extra contamination sources, and the limitation of available filtration media for particle deposition.

Sublimation offers an alternative to filtration for the recovery of particles from snow or ice. With sublimation, one may achieve good particle recovery, introduce only minimal sources for sample contamination, deposit particles on any type of surface, and maintain the sample in a frozen state during the process. The negative aspects of sublimation are the need to purchase or build an expensive freeze dryer and the relatively slow sublimation process. Sublimation has been used to recover gases from snow and ice (Wilson and Donahue 1990; Wilson 1995). However, it is not used often for particle recovery. At NIST, we use a Labconco FreeZone® model 77530¹ freeze dry system for

¹ Commercial equipment, instruments, materials and software are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement of these items by NIST, nor does it imply that they are the best available for the purpose.

sublimation. Within the drying chamber, we use an additional buffering device to enhance particle recovery. Without the buffering device, particle recovery is only *ca.* 60%. When a snow or ice sample is placed within the buffering device, particle recovery is 100%. Figure 1 illustrates the sublimation buffering device. It slows the sublimation process, thus reducing the turbulence around the sample and subsequent particle loss. The disadvantages of using the sublimation buffer is that sample size is limited to *ca.* 100 ml (due to the size of the sublimation buffer) and that sample sublimation time is increased by *ca.* 50%

Evaporation may be used, however infrequently, for particle separation from snow and ice. Even though evaporation may seem simple and inexpensive, particle loss is difficult to control and evaporation at higher temperatures may cause changes in particle chemistry.

Analysis of ^{14}C in Snow Particles with AMS

Clayton *et al.* (1955) introduced the idea of using atmospheric radiocarbon to discriminate between fossil and biospheric sources. This idea relies on the absence of ^{14}C in fossil fuel and the presence of ^{14}C in the biosphere. The radioisotope, ^{14}C , is employed as a tracer for vegetative emissions such as forest fires, field and slash burning, and natural emissions. The AMS revolution brings the state of technology to the point where only micrograms of carbon are required for analysis (Currie *et al.* 1994). In recent years, this method has been utilized to determine the contemporary sources of aerosol carbon in urban areas (Currie *et al.* 1994; Cooper *et al.* 1981; Hildemann *et al.* 1994). This work is the first attempt to apply AMS measurements to particles contained in snow.

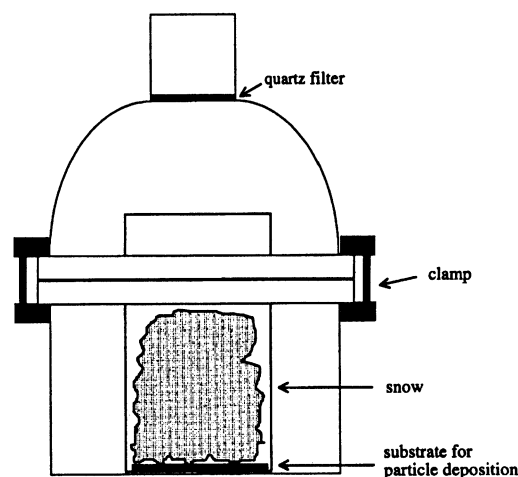


Fig 1. Buffer used to eliminate particle loss during sublimation

For a feasibility study, two urban snow samples were analyzed for ^{14}C . The snow was collected in Gaithersburg, Maryland after a large snowfall on January 8, 1996. The purpose of this exercise was to test the procedure on a snow sample with large amounts of particulate carbon before moving to samples from remote areas with smaller carbon particulate concentrations. Table 1 shows the sample size, mass of particles recovered, and the mass of total particulate carbon recovered. The Urban Dust SRM (SRM 1649) was run in parallel with the samples for quality control purposes. A blank Al foil sample was also run. Note that the carbon mass recovered for AMS in the Al foil blank is higher than the mass of carbon determined by the CHN analyzer. This indicates that the CO_2 trapping process adds carbon to the total blank. Optimizing the seals of the trapping system can reduce this value.

The procedure started by using sublimation to deposit particles on Al foil from Gaithersburg snow. Silica disks, Al foil, Sn Foil, Ag foil and Fe foil also were investigated as suitable substrates for particle deposition. We found Al foil to be a good medium. It is inexpensive, easily handled and can be cleaned to the point where the carbon blank is small with respect to other media. Sublimation of the snow from the particles was performed in the sublimation buffer, described above, within the drying chamber of the freeze dryer. Snow was sublimed for each of the two samples (25.7 g and 22.7 g). After sublimation, the Al foil was folded several times to prevent the loss of any particles. Sample handling was performed in a clean bench utilizing tweezers to minimize the chance of sample con-

TABLE 1. Sublimation of Gaithersburg, Maryland Snow for ^{14}C Analysis

Sample	Mass of snow (g)	Mass of particles (μg)	Mass of carbon (μg)	Carbon mass recovered for AMS (μg)
1	$25.7 \pm 0.1^*$	470 ± 2	140.7 ± 1.5	136.9 ± 4.1
2	22.7 ± 0.1	531 ± 2	158.6 ± 1.5	152.5 ± 4.6
1649 SRM	N/A	N/A	96.0 ± 1.0	92.77 ± 2.9
Al foil blank	N/A	N/A	1.38 ± 0.1	4.49 ± 0.18

*Uncertainties reflect the authors' best estimates of 1- σ uncertainty bounds.

tamination. The Al foil, both before and after sublimation, was weighed so that the deposited particle mass could be determined.

The samples were analyzed for total carbon with a Fisons CHN analyzer model EA 1110 (CE Instruments 1996). First, the CHN analyzer combusts a sample at temperatures in excess of 1500°C to oxidize all carbon in a sample. Qualitative oxidation is achieved by passing the combustion gas mixture through an oxidation catalyst (CrO_3) zone (1.5 cm diameter by 9.5 cm long) at a flow rate of 1 ml s^{-1} . The combustion gas mixture is then passed through magnesium perchlorate (0.2 cm diameter by 8 cm long) to remove water and then eluted and separated by a Porapak[®] PQS column. A therm conductivity detector then detects the CO_2 as it emerges from the column. Upon exit from the CHN analyzer, the CO_2 gas is trapped with liquid nitrogen. The liquid nitrogen trap only has a 97% trapping efficiency. However, mass spectrometry results indicate that minimal isotope fractionation occurs. The CO_2 gas is transferred to reduction tubes and AMS targets are prepared utilizing the method developed by Verkouteren (Verkouteren, Klinedinst and Currie 1997; Klinedinst *et al.* 1994; Verkouteren and Klouda 1992; Verkouteren *et al.* 1987).

AMS was performed on the snow particle samples at the Institute for Radium Research and Nuclear Physics in Vienna, Austria. Results show that the fraction of modern carbon (f_M) in the Gaithersburg snow is *ca.* 1.2. This should be taken as a demonstration of method feasibility and not as absolute characterization of the f_M in Gaithersburg snow. This f_M value suggests active residential wood burning during the snow event. This snow event was very large, so the vehicular traffic source of carbon should be very minimal. Currie *et al.* (1996) indicates that a f_M value of 1.2 would result from the burning of *ca.* 20-yr-old trees.

The use of this procedure on urban snow demonstrates the feasibility of applying this technique to snow from more remote locations. Sample size possibly will be a limiting factor, so future research will focus on reducing the carbon blank.

Analysis of Particles in Snow Utilizing the Laser Microprobe Mass Spectrometer

The laser microprobe used is the LAMMA 500 (Denoyer *et al.* 1982; van Vaeck *et al.* 1993; Kaufmann 1986). Applications for particle analysis have been reported (Wieser *et al.* 1981; Wieser and Wurst 1986; Otten, Bruynseels and van Grieken 1987; Bruynseels *et al.* 1988) and particle source apportionment (Currie *et al.* 1989; Surkyn *et al.* 1983). The LAMMA 500 is composed of a dual laser system coupled to a time-of-flight mass spectrometer through an optical microscope. The sample is viewed optically and a particle is selected for analysis by aiming a co-aligned pilot laser beam spot (from a HeNe laser) onto the particle. The ionizing laser is a high power, pulsed, frequency quadrupled, Nd:YAG laser that provides pulsed UV radiation (266 nm). It is focused on the sample by an optical microscope objective. All ions generated are accelerated to uniform translational energy

and mass-separated by time-of-flight (TOF) mass spectrometry. The arrival of the ion packets at the end of the drift tube is determined by a secondary electron multiplying detector.

The instrument has transmission geometry that is optimized with the laser beam and the mass spectrometer in-line. The laser microprobe has 1–5 μm spatial resolution, high-detection sensitivity and detection capability for either positive and negative ions produced during the laser ionization. In most sample matrices, the alkali metals are most easily detected and are reported to have a detection limit on the order of 10^{-19} g (Kaufmann 1986). Most other elements have detection limits between 10^{-17} and 10^{-19} g, allowing detection of minor and, in some cases, trace elements from a single particle with micrometer dimensions and picogram mass.

Particulate samples were prepared by the sublimation of snow onto fused silica coverslip substrates that can be mounted directly into the laser microprobe. The LAMMA 500 requires optically transparent substrates or thin films because the beam must penetrate through the substrate to ionize the sample. Gaithersburg snow was analyzed first to determine the feasibility of using LAMMA for snow particle analysis. Small amounts of the Gaithersburg snow provided substantial particle deposits (by LAMMA standards). Only *ca.* 3 g of Greenland snow was needed for the LAMMA analysis.

For the snow samples from Summit, Greenland, individual and groups of particles were analyzed. Both positive and negative ion mass spectra were obtained. The resulting positive ion mass spectra contained peaks that indicated the presence of Li^+ , C^+ , Na^+ , Mg^+ , Al^+ , Si^+ , K^+ , and Ca^+ . In the negative mass spectra, peaks were observed that correspond to O^- , F^- , C_n^- , C_nH_m^- , Cl^- , NO_3^- and Si_nO_m^- . Carbon was found in the negative ion mode in conjunction with hydrogen forming the C_nH_m complex indicative of pyrolyzed organic compounds or hydrogenous carbonaceous soot. No identifiable organic molecular ions were detected. Sulfate, for the most part, was not observed to be present. Carbonate may be present at m/z 60; however, there is a mass interference from C_5^- and SiO_2^- . Si related peaks can be derived from either the particles or from the silica substrate. A summary of the cations and anions determined in Greenland snow is reported in Table 2.

Examples of time-of-flight spectra are presented in Figure 2 for positive ions and Figure 3 for negative ions. The positive ion spectra are very similar to that reported by Bruynseels *et al.* (1988) for North Sea aerosol. The peak assignments for the larger m/z peaks are consistent with their work, but inconsistent with our negative ion results since no sulfate or carbonate was conclusively found. The negative ion spectra illustrate the presence of hydrogen-containing carbonaceous particles.

TABLE 2. Frequency of Occurrence for Cations and Anions in the Laser Microprobe Mass Spectra for Summit, Greenland Snow

Cation	Times observed	Total spectra analyzed	Anion	Times observed	Total spectra analyzed
Li^+	11	17	O^-	24	24
C^+	4	17	F^-	6	24
Na^+	13	17	CN^-	24	24
Al^+	14	17	C_nH_m^-	23	24
Mg^+	2	17	Cl^-	22	24
Si^+	8	17	NO_3^-	8	24
K^+	10	17	Si_nO_m^-	18	24
Ca^+	9	17			

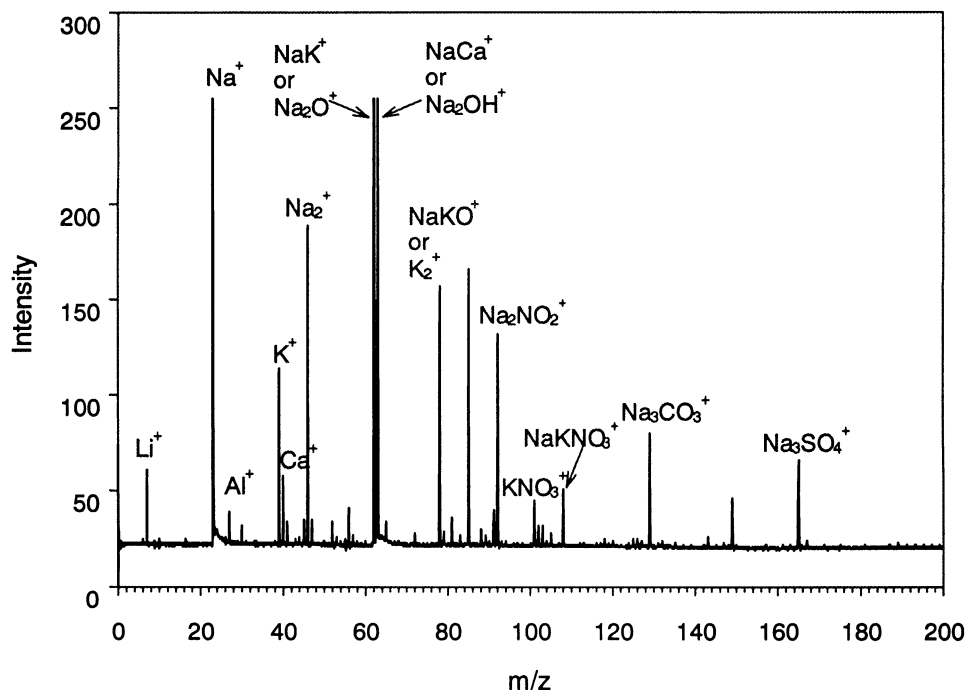


Fig. 2. LAMMA positive ion time-of-flight spectrum (snow sample from Summit, Greenland). Note that these are not absolute assignments and could be other ions.

CONCLUSION

Our study has demonstrated that carbonaceous particles in snow can be analyzed for ^{14}C . However, carbon levels in Arctic snow and ice may require the use of filtration rather than sublimation for particle recovery from snow due to the large volumes of ice or snow required in obtaining sufficient particles for carbon analysis. The specific application of the AMS sample preparation methodology presented here is currently best suited for analysis of snow from regions more polluted than the Arctic. Depth profiling of ice cores from lower latitude glaciers would be ideal for this methodology. Filtration of Arctic snow samples and the subsequent analysis for ^{14}C by AMS are reported by Currie *et al.* (1998). The sample mass required for LAMMA is very small, indicating that this technique can provide good time resolution in ice cores, and also serve as a soot carbon screening method for larger samples. LAMMA analyses of particles contained in Greenland snow produced results for multiple ions in the time-of-flight spectra. We project that source apportionment techniques, such as those used by Currie, Fletcher and Klouda (1989), may be applied to LAMMA results on snow particles to attain information on the origin of historic Arctic aerosols.

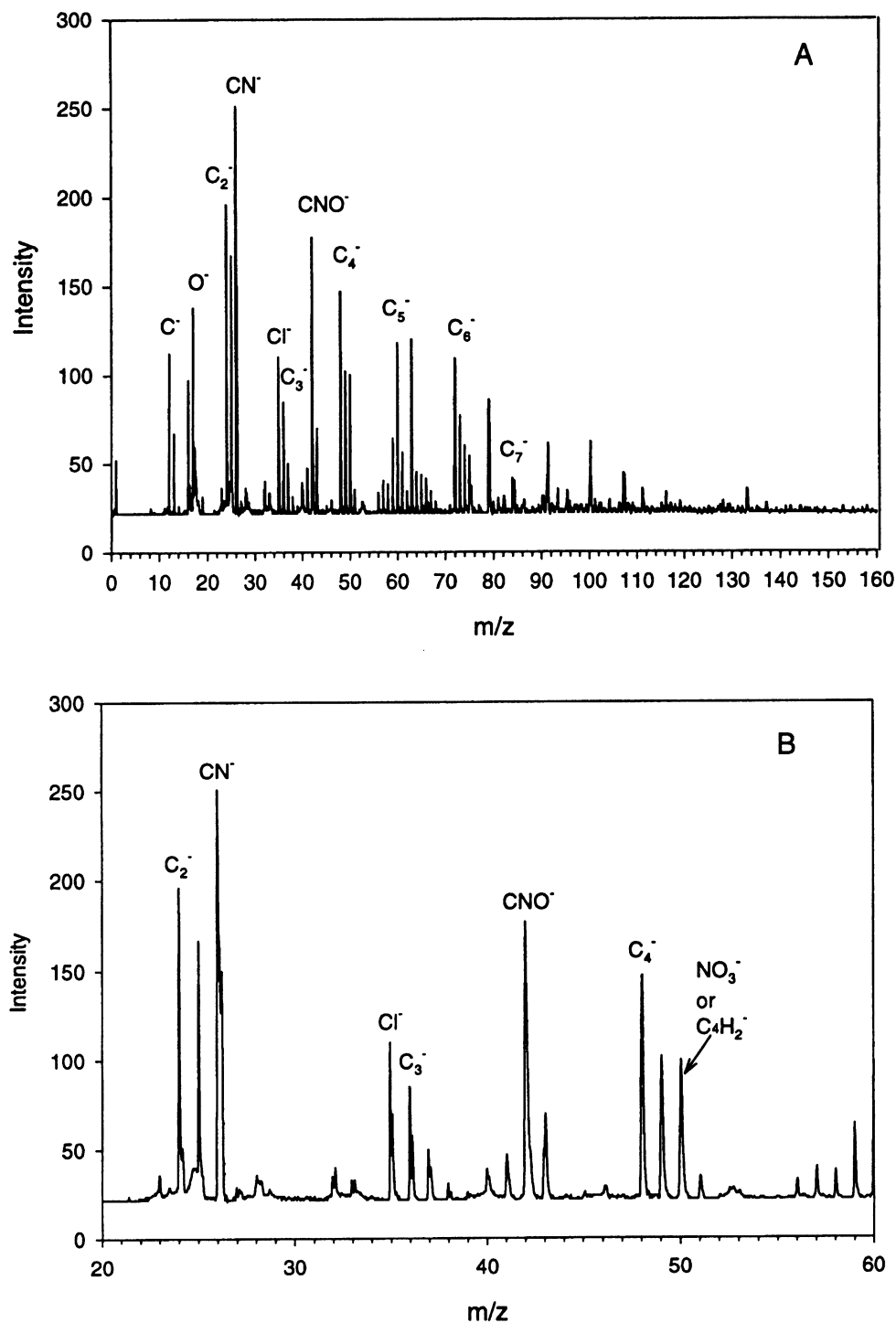


Fig. 3. A. Full LAMMA positive ion time-of-flight spectrum (snow sample from Summit, Greenland). B. LAMMA negative ion time-of-flight spectrum zoomed into the region between 20 and 60 m/z (snow sample from Summit, Greenland). Note that these are not absolute assignments and could be other ions.

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