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AMS MEASUREMENTS OF SOUTH AMERICAN RAINWATER SAMPLES *

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Accelerator mass spectrometry (AMS) is one of the most powerful applications of heavy-ion beams in fields not directly related to nuclear physics basic research. The development of this highly sensitive technique at the electrostatic accelerator of the TANDAR laboratory has recently been accomplished. Aiming at environmental applications of our AMS activities, we have established a research program using the long-lived radioisotope ^{36}Cl as an atmospheric tracer, in cooperation with the AMS group of the Technical University of Munich. The subject of the investigation was the global fallout of ^{36}Cl and its latitudinal distribution. Precipitation samples were collected at different latitudes in Argentina, Chile, and Antarctic, covering a range from 24°S to 62°S. The resulting ^{36}Cl/Cl ratios varied from 1×10^{-14} to 62×10^{-14}. Systematics studies of this radioisotope may provide a monitor for atmospheric releases (anthropogenic contribution) and a baseline for natural ^{36}Cl concentration.

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1. The Accelerator Mass Spectrometry technique

In this contribution we present the development of the Accelerator Mass Spectrometry (AMS) technique at the TANDAR laboratory in Buenos Aires, and, as an example of its application, the results of measurements of the atmospheric tracer chlorine 36 in rainwater samples.

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AMS is a very sensitive technique which is capable of tracing long-lived natural and artificial radionuclides at extremely low concentrations, defined as the ratio of the rare radioisotope to a stable isotope, which lies in the range of 10^{-10} to 10^{-16} (see [1]). Of particular interest are those radioisotopes produced in the atmosphere which can be used as tracers in environmental research. Since the half-lives of some of these radioisotopes range from several thousand to million years (see Table I), they can not be measured through radioactive decay counting, where only few decays occur in any reasonable measuring time. Instead, AMS offers the alternative of counting each individual radioisotope in a nuclear particle detector. In this respect it is important to note that the essential feature of this technique is that the particles to be detected are accelerated to energies approximately three orders of magnitude greater than those used in conventional mass spectrometry. At these energies a variety of identification and detection procedures derived from nuclear physics can be applied to reduce background problems which limit the sensitivity.

TABLE I

Long-lived radioisotopes measured routinely with accelerator mass spectrometry

Isotope	Half-life(years)	Stable Isotopes	Stable Isobars
^{10}Be	1.6×10^{6}	^{9}Be	^{10}B
^{14}C	5730	^{12,13}C	^{14}N
^{26}Al	7.16×10^{5}	^{27}Al	^{24}Mg
^{36}Cl	3.01×10^{5}	^{35,37}Cl	^{36}Ar,^{36}S
^{59}Ni	7.5×10^{4}	^{58,60,61,62,64}Ni	^{59}Co
^{129}I	1.57×10^{7}	^{127}I	^{129}Xe

Our AMS program is running at the electrostatic accelerator of the TANDAR laboratory [2, 3]. Figure 1 shows a schematic view of the accelerator and its main components. Small samples containing few milligrams of material are loaded in an ion source from which negative ions of the radioisotope to be investigated are extracted. The ions pass through a high-resolution injection magnet for a first mass analysis and are preaccelerated to about 150 keV to the accelerator tank. Then, they are accelerated to the high-voltage terminal, which can be held at a positive voltage of up to 14 MV. An electron stripper at the terminal (a thin carbon foil) removes several electrons and therefore the ions change their polarity from negative to positive. Positive ions are then accelerated again to ground potential. Another important function of the stripper is the dissociation of molecular ions. In this way, molecules with the same mass of the ion of interest, and therefore accepted by the injection magnet, are eliminated. The high-energy analysing magnet removes scattered particles accepted by the injection analyzer, molecular fragments and unwanted charge states. The ions are transported further on to the detection system where the radioisotope counting rate is measured directly in the detector.

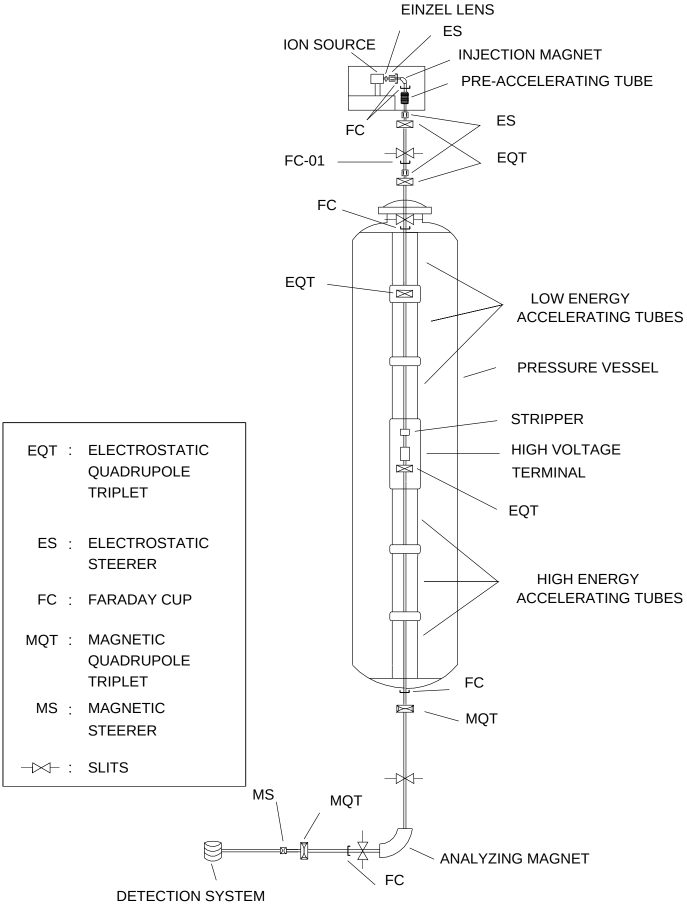

Fig. 1. Schematic view of the TANDAR accelerator showing its principal components.

2. ^{36}Cl measurements from precipitation samples

One of the first goals of our AMS program is the measurement of the global fallout of the cosmogenic ^{36}Cl isotope in South America. This research program has been carried out in collaboration with the Technical University of Munich, Germany. The ^{36}Cl radioisotope, with a half-life of 3×10^5 years, has two stable isotopes (chlorine 35 and 37, with 76% and 24% of natural abundance, respectively), and there are also two stable isobars of mass 36, namely ^{36}Ar and ^{36}S. Since negative ions of argon can not be formed, this element is not present in the acceleration process, and, therefore, it does not contribute to the background. The only isobaric contamination comes from sulphur-36. This selection in the ion formation is one of the main advantages of AMS.

The hydrophilic nature of ^{36}Cl makes this radioisotope a well suited tracer to study atmospheric transport processes from precipitation samples. This long-lived radionuclide is continuously produced in the atmosphere, approximately two thirds in the stratosphere and one third in the troposphere, mainly by spallation reactions induced by cosmic rays on argon [4]. After residing for 1–2 years in the stratosphere, the ^{36}Cl radioisotopes are transported to the troposphere, where their residence time varies from a few days to weeks. The atoms of ^{36}Cl associated with aerosols reach the Earth surface by wet (washed out by precipitation) and dry deposition. The production of ^{36}Cl in the stratosphere depends on the geomagnetic latitude because the cosmic ray particles are influenced by the Earth's magnetic field. As the shielding effect decreases from the equator to the poles, then the maximum amount of ^{36}Cl is present at the poles. Nevertheless, the latitudinally averaged deposition rate is strongly influenced by the injection of stratospheric air masses into the troposphere, a process that occurs, mainly, at mid-latitudes [5]. Therefore, the ^{36}Cl fallout is expected to exhibit a pronounced dependence on the latitude, with a mid-latitude peak.

The existing models of ^{36}Cl production, however, underestimate the measured deposition of this radioisotope. In particular, studies of ^{36}Cl precipitation in the northern hemisphere yield concentration values higher than those expected from natural production [6]. The reason for this discrepancy is not well determined and several recent experiments have examined the possible anthropogenic contribution to the ^{36}Cl production. This contribution comes, mainly, from thermal neutron activation on ^{35}Cl produced during nuclear-weapon tests. Therefore, chlorine-36 ions are injected into the stratosphere following from there the atmospheric circulation.

In order to complete the rather scarce information on the ^{36}Cl fallout in the southern hemisphere we measured ^{36}Cl concentrations from precipitation samples collected at different latitudes in Argentina, Chile, and the

Antarctic, covering a latitudinal range from 24°S to 62°S. This are the first ^{36}Cl measurements reported from South American precipitation samples.

3. Experiment

3.1. Sample collection and preparation

Samples were collected in Ushuaia (54.48° S, 68.18° W), Bahía Blanca (38.43° S, 62.17° W), and Jujuy (24.11° S, 65.18° W), Argentina, in Santiago (33.27° S, 70.40° W), Chile, and in the Antarctic (62.20° S, 58.53° W).

The precipitations from Jujuy and Ushuaia were collected monthly (the first one from January 1988 to January 1989 and the second one from January 1988 to December 1989), containing the respective sample to be studied the same amount of water from each month. Bahía Blanca's sample was collected during April 1993. The sample from Santiago was obtained from precipitations that occurred between May–June 1996 and they were handled identically to those obtained in Ushuaia and Jujuy. The Antarctic sample was collected between February and March 1995. The volume of the samples ranged between 1 and 2 litres. The sample collected at the Antarctic site consisted only of wet-precipitation, whereas the other four samples contained bulk (wet and dry deposition) precipitations.

The chemical preparation of the material proceeded as follows [7]: H_2O_2 was added to the sample to eliminate any kind of micro-organisms present there. At least three months after adding H_2O_2, 50 ml were taken from each sample to measure the concentrations of stable Cl^- and SO_4^{2-} by ion chromatography. The amount of Cl expected in the total volume of the sample was calculated and, if this quantity was less than 4 mg of Cl, a natural NaCl carrier (*i.e.* without ^{36}Cl) from Bad Reichenhaler salt (taken from a deep mine in the south of Bavaria, Germany) was added to the sample. The remaining water was filtered and concentrated to approximately 70 ml. The concentrated water was acidified by HNO_3. Silver chloride was precipitated with excess of $AgNO_3$ and separated by centrifuging. To minimize the contribution to the background from stable ^{36}S in the ^{36}Cl determination, the AgCl precipitate was dissolved in NH_4OH and sulfates were removed by addition of $Ba(NO_3)_2$ to precipitate $BaSO_4$ [8]. Then, the remaining water was acidified and AgCl was precipitated again. AgCl was dried in an oven at 60°C. This chemical technique was also followed to prepare blanks from the same natural NaCl salt used as carrier material and using bidistilled water. Three different blanks with $^{36}Cl/Cl$ ratios of $(4.5 \pm 1.5) \times 10^{-14}$, $(6.2 \pm 4.4) \times 10^{-15}$ and $(2.1 \pm 1.7) \times 10^{-15}$ were made.

3.2. AMS measurements

Several measurements were carried out at the Munich MP tandem accelerator and at the 20UD accelerator at the TANDAR laboratory. At the first laboratory, the detection and identification of the particles were done at the dedicated Gas-filled Analyzing Magnet System (GAMS) of the Munich accelerator [9]. It consists of a 135° magnet followed by a Frisch-grid ionization chamber. In this chamber, the anode is divided into five energy-loss sections; two of these sections, the first and the third ones, are triangle-shaped zones which make it possible the determination of the angle and of the entrance position of the incoming particles. A total energy signal was taken from the Frisch grid. For the chlorine measurements the gap inside the magnet was filled with nitrogen at a pressure of 9 mbar which optimizes the position resolution. The ionization chamber was filled with isobutane at a pressure of 52 mbar.

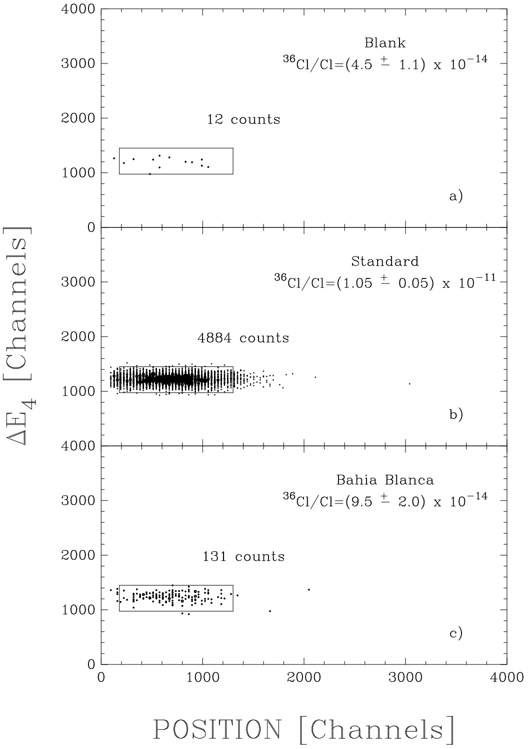

Fig. 2. Position against ΔE_4 gated spectra for different samples: (a) — a blank measured during 222 s; (b) — a standard sample measured during 150 s; (c) — a Bahía Blanca sample measured during 1198 s.

The chemical treatment of the samples reduced the sulphur contamination by a factor of about 20. However, a remaining sulphur contamination due to sputtering on the cathode holders (Cu holders in our case) was also present and usually causes a higher counting rate in the final detector than the chemically purified sample [10]. Although the ^{36}S isobar entering the GAMS with the same energy as the ^{36}Cl ions was bent out of the detector, there was still a tail of degraded sulphur particles reaching the detector that was clearly resolved from the ^{36}Cl events in the position versus ΔE_4 (fourth energy-loss section) bidimensional spectrum. For this reason, the ^{36}S contributions to background as well as possible interferences of stable chlorine ions were rejected by software analysis. As an example of the gated spectra, Fig. 2 shows position against ΔE_4 events from a blank in Fig. 2(a), from a standard in Fig. 2(b) and from a precipitation sample in Fig. 2(c). In the first case, the spectrum was accumulated during 222 s, whereas the accumulation time in the case of the standard sample was 150 s and in the precipitation case was 1198 s. The normalization of these runs was done with a ^{37}Cl beam, whose intensity at the entrance to the tandem was $1.86\,\mu$A, $3.39\,\mu$A and $2.15\,\mu$A, for the blank, the standard and the actual sample, respectively.

Two standard samples having ^{36}Cl/Cl ratio values of 1.1×10^{-11} and 7.6×10^{-13} have been used for calibration purposes. The AMS measurements were performed in the following way: after three unknown samples a standard probe was measured to check the stability. Moreover, a blank was measured every 5 or 6 runs to monitor the background level. A given sample was measured at least three times and each run lasted about 300 seconds.

Memory effects have been estimated to be less than 2×10^{-3} by sputtering the 7.57×10^{-13} standard during 25 min with $1.0\,\mu$A of ^{35}Cl and quickly replaced it with one blank, which was measured during 52 min having a ^{35}Cl current of $1.23\,\mu$A.

4. Results and discussions

The measured ^{36}Cl/Cl ratios and ^{36}Cl concentrations as well as the chlorine and sulfates (after the chemical treatment) obtained for each sample are given in Table II. Systematic errors of 10% were estimated for carrier, current and rainfall measurements, whereas the rest of the errors was taken to be statistical.

As shown in Table II, the ^{36}Cl/Cl ratios for the precipitation samples range from 1×1^{-14} to 62×10^{-14}. The Cl concentrations are between 1 and 3 ppm for all samples except the Antarctic one whose value was 66 ppm. The huge chlorine concentration value obtained for this site might be due to the fact that the sample was taken from a peninsular region

TABLE II

Chlorine and sulfate (after the chemical treatment) concentrations, ^{36}Cl/Cl ratios and ^{36}Cl concentrations for the different collection sites.

Site	Latitude	Cl [ppm]	SO_4 [ppm]	^{36}Cl/Cl [$\times 10^{-15}$]	^{36}Cl at/l [$\times 10^6$]
Jujuy	24.11°S	2.7 ± 0.60	< 0.01	620 ± 130	31 ± 9
Santiago	33.27°S	1.45 ± 0.05	< 0.20	115 ± 30	2.8 ± 0.6
Bahia Blanca	38.43°S	1.80 ± 0.05	< 0.02	95 ± 20	3.2 ± 0.7
Ushuaia	54.48°S	3.3 ± 0.50	?*	250 ± 70	15.2 ± 4.8
Antarctic	62.20°S	66 ± 5.00	< 0.30	10.4 ± 5.5	6.1 ± 3.2

* It was not possible to measure the concentration of sulfates in the Ushuaia sample.

where the chlorine concentration is significantly high. The ^{36}Cl/Cl ratios are, in general, comparable with those measured in the northern [11,12] and southern [13] hemispheres where values ranging from, approximately, 3 to 40×10^{-14} were obtained (Ref. [11–13]) and lower than those reported by Cornett *et al.* [6], who measured ratio values up to about 3000×10^{-14} at 46° N.

In the cases of the samples from Santiago, Bahía Blanca and Antarctic it is not correct to directly compare the ^{36}Cl concentrations (or fallout) with the Lal and Peters [4] predictions because these samples were collected monthly or daily, and therefore, they might have seasonal variations. Different measurements performed in the northern [11] and southern [13] hemispheres showed seasonal variations of the ^{36}Cl concentration, which in some cases are of one order of magnitude. In addition to that, for the case of Santiago the relatively high value of ^{36}Cl fallout could, probably, arise from the neighbourhood (approximately 6 km) of a nuclear reactor to the site of the sample collection.

In the case of Jujuy and Ushuaia, where the precipitations were collected over more than a year and the samples were prepared by mixing a given amount of the monthly precipitation, the seasonal dependence is averaged in the result. For more definitive conclusions one needs additional measurements, from another sites, taking extreme care in the collection of the precipitation samples and collecting them over longer period of time. Such systematic studies will also allow to follow possible seasonal variations.

Summarizing, during the last few years we devoted our efforts towards the development of the AMS technique in a large nuclear physics facility, the 20MV tandem accelerator at the TANDAR laboratory. This technique imposes stringent requirements on different parameters of the accelerator, for example, high efficiency of the ion source and large and steady beam transmission (which implies stability of the high voltage terminal and of the ion optic devices) and therefore a considerable amount of work has been dedicated in this direction. The AMS technique, which finds application in a large variety of disciplines, was born from nuclear physics and it still has a close relationship to it. Not only because it uses the same detection and identification techniques but also because it requires the knowledge of nuclear physics information such as relevant cross sections, half-lives.

Much more work has to be done for the use of this radionuclide in environmental applications. Systematic measurements of ^{36}Cl is required to gain an insight of the interplay between its two principal sources (anthropogenic and cosmogenic), in space and time. Finally, we would like to remark the importance of ^{36}Cl for several hydrological purposes, like as ground water tracer, which is of interest for assessing potential sites for disposal of radioactive waste.

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