Abstract

This report is based on the study of ^{22}Na in the atmospheric air, is focused to know the seasonality of this radionuclide, compare it with another cosmogenic radionuclide, check the efficiency of the applied detection system and propose another method in order to improve the presently used method.

This isotope can be used as an atmospheric tracer and can provide information about many atmospheric processes, in particular on the exchange of air between the stratosphere and the troposphere.

In this document it is included basic information on the characteristics of ^{22}Na and its origin as well details on the instrumentation and methodology that have been applied.

In this document is also explained how has been improved the existent method to detect and quantify the ^{22}Na, it can be applied even during cold seasons in order to detect and quantify the ^{22}Na when the concentration of this radionuclide is really low with a mean value around 0,5 $\mu Bq/m^3$ in summer and around 0,1 $\mu Bq/m^3$ in winter.

Contents

1. Glossary

^{22}Na: It is a radioactive isotope of sodium, with a half-life of 2,6029 years.

^{22}Ne: It is a noble gas. It is a stable isotope.

^{38}Ar: It is the main stable isotope of argon which is present in the atmospheric air in a variable of concentration, ~0,98 % at the sea level.

Becquerel (Bq): Is the SI derived unit of radioactivity, equivalent to a disintegration per second, named after who discovered the radioactivity.

CSN: Nuclear Safety Council.

Cosmogenic isotope: In the upper atmosphere several radioactive isotopes are being produced when cosmic rays collide with atmospheric molecules at high speed. These isotopes are known as cosmogenic isotopes **[10].**

d.p.m.: Disintegrations Per Minute or Becquerel multiplied by 60.

ETSEIB: School of industrial engineering of Barcelona.

EURATOM: European Atomic Energy Community.

INTE: Institute of Energy Technologies.

LARA: Radioactivity Analysis Laboratory of the INTE-UPC.

MDA: Minimum detectable activity.

UPC: Universitat Politécnica de Catalunya (Polytechnic University of Catalonia)

Stratosphere: Is the second major layer of Earth's atmosphere, just above the troposphere, and below the mesosphere. It is situated between about 10–13 km and 50 km altitude above the surface.

Troposphere: Is the lowest portion of Earth's atmosphere is approximately 17 km in the middle latitudes.

2. Preface

In this part is going to be all the basic information about the project such as the aims and the scope of the study.

2.1. The origin of the project and motivations

In 1985, Spain adhered to the treaties that constitute the European Communities and in January 1st 1986 Spain became an European Communities Member State. From this moment, international and national legislation applicable in Spain is accomplished according to the rules of the European Union. Moreover, Spain is a Member State of the IAEA and of the OECD/NEA, whose constitutive treaties, conventions and additional treaties have been ratified. In particular, Spain adhered to the EURATOM (European Atomic Energy Community) treaty in 1996.

The EURATOM articles 35 and 36 establish that each member of the EURATOM must have the necessary facilities for checking-up the levels of radiation in the air, water and soil and this regional organizations have to communicate those levels periodically to the EURATOM. Each member state should define representative geographical regions for its own territory. Within the EURATOM framework the sparse network was born as a monitoring network comprising for every region and for every sampling medium at least one location representative of that region. At such locations high sensitivity measurements should be performed thus giving a transparent representation of actual levels and trends of radioactivity. Spain has been divided into 5 regions in which must be monitored the air (among other sample types) with a high precision. There is a low number of facilities of such type because the instrumentation and procedures for detecting and quantifying the radionuclides of interest are really expensive **[22].**

Figure 1.Europe divide in regions by EURATOM at 2000.

The CSN (Nuclear Safety Council) is the Spanish regulatory body, the responsibilities of the CSN include that of supervising the measures for the radiological protection of the public and the environment, as well as controlling and monitoring. Within this framework, the CSN

manages the National Radiological Surveillance Network consisting of automatic and sampling stations. Among other sampling stations, the CSN manages the sparse network through collaboration agreements with universities and research organisations throughout the country.

One of those facilities is located at the INTE (Institute of Energy Technologies) and the aerosol collector for atmospheric monitoring is placed on the roof of these facilities. According to the established contract, the INTE has to share the report of the analysis of the air to the CSN in order to check up the levels of radionuclides in the air. As a cosmogenic isotope the ^{22}Na does not have to be reported but it is interesting as atmospheric tracer and it can provide us information about the movement of masses in the atmospheric air, in particular about the air exchange between the stratosphere and troposphere.

Even in such high-precision sampling stations, nowadays, it is not easy to quantify the levels of ^{22}Na several weeks each year because its atmospheric concentration it's too small for being detected well enough to quantify it. We are going to measure in the order of decimals of $\mu Bq/m^3$ or $10^{-7}Bq/m^3$. Many previous scientific works of other authors pointed out this problem **[1 to 9]**.

2.2. Aims

This project has been orientated for tuning up a measurement method for ^{22}Na in the atmospheric air at the LARA INTE-UPC facilities. According to this, the following aims have been proposed:

- Study the temporal evolution of ^{22}Na at ground level and correlate it with other variables: Solar cycle, precipitation, wind flow, temperature and many another possible variables that will be found.
- Propose a method to optimize or improve the detection of ^{22}Na at the INTE facilities.

2.3. Scope

To study the temporal evolution of ^{22}Na in Barcelona, the project is going to be based on the available results from year 2005 to year 2015. Since 2001, the Radioactivity Analysis Laboratory (LARA) collects in a weekly basis filters from a high-volume dust sampler that are analysed using gamma spectrometry detectors. As it has been already mentioned, the ^{22}Na it is not reported to the CSN, and thus, the project will include the necessary work to compile and assess the ^{22}Na content in this filters.

3. Introduction

In this part is going to be presented some basic information on radioactive ^{22}Na characteristics, and influence factors on it atmospheric concentration.

3.1. Radioactivity

Radioactivity is the process of spontaneous decay and transformation of unstable atomic nuclei accompanied with the emission of nuclear particles and/or electromagnetic radiation (also referred to nuclear radiation). It was discovered by Becquerel in 1896 and it marked the start of the study of atomic nucleus, it also constitute the first step in acknowledge of the nuclear structure.

After several years of research it was found that radioactive nuclides were able to emit one or more kinds of radiation and they can be classified according to its penetrability:

- α rays (nucleus of ^4_2He) can be absorbed by one sheet paper,
- β rays (electrons or positrons), can be necessary put a 1 cm thick PMMA layer to stop them.
- γ rays (electromagnetic radiation), can be necessary use thick layers of lead to reduce its intensity.

The radioactivity is an aleatory phenomena, if the probability of the disintegration of one nucleus in a sample is P(t) in the time dt, and N(t) is the number of radionuclides in this sample, then their dependence with time can be expressed as follows:

$$P(dt) = \lambda\, \mathrm{dt} \quad (1)$$

$$N(t) = N_0 \cdot e^{-\lambda \cdot t} \quad (2)$$

Where λ is the radioactive decay and it is expressed as [unit time]$^{-1}$, for example [min]$^{-1}$.

3.2. Cosmic radiation

The cosmic radiation is the radiation that consists of particles with an extraterrestrial origin (with a huge quantity of energy) that interact with the particles present at the atmosphere **[14]**.

Cosmic-ray particles both refer to primary energetic particles of extra-terrestrial origin that strike the Earth's atmosphere and to secondary particles generated by their interaction with the atmosphere. Primary particles are attenuated in the upper atmosphere. Reactions take place in the upper part of the atmosphere and generate secondary particles. The cosmic radiation field at the ground altitude (0-3km) consists almost entirely of secondary particles.

The primary cosmic-ray flux at the Earth's orbit has two components: galactic cosmic ray (GCR) and solar cosmic ray (SCR).

The GCR is a mixture of ~87 %protons, ~12 % alpha particles and ~1% of heavier nuclei with atomic number from 3 to ~90.The GCR has a production ratio of 4 nucleons cm^{-2} s^{-1} and only the solar modulation cause a variability of the observed GCR variability with a range of energy ($E<1$ GeV·$nucleon^{-1}$) and it increases by one order of magnitude with the interaction of GCR with magnetic fields connected with the solar-wind plasma.

The SCR consists of 98 % protons and 2 % heavier nuclei. Their energies typically ranged between 1-100 MeV. The total flux is subjected to strong temporal variations but its average value being around 75-100 nucleons cm^{-2} s^{-1}. Because their relatively low energies, they can only cause nuclear reactions at high latitudes (above 60º N or S) and even there the production is restricted to the very top atmosphere. The Earth's magnetic field shields against cosmic radiation reducing the amount that reaches Earth's surface. Primary cosmic rays incident to the top of atmosphere are protons with energies nearby 1 GeV. These primary rays generates the secondary rays because interact with the upper atmosphere, thus secondary rays consist mainly in neutrons and muons with high kinetic energies (up to many GeV), they reach the Earth's surface before they decay.

After production the nuclides are subjected to different processes according to their geochemical properties. For example the ^{14}C is oxidised to CO_2 and ^{22}Na becomes attached to aerosols. Then they are spread out from the site of production following the trajectories of the air masses until a part of them becomes stored in natural reservoirs or they disintegrate. Because of the thermal structure of the tropopause, the residence time of aerosol in the stratosphere is between 1 and 2 years. The concentration of the cosmogenic nuclides at a specific site is strongly dependent on the local precipitation rate. **[15]**

3.3. ^{22}Na properties and origin

A spallation reaction is a process where a light projectile (proton, neutron, or light nucleus like muons), with kinetic energy from several hundreds of MeV to several GeV, interacts with a heavy nucleus (e.g., lead) and causes the emission of a large number of hadrons (mostly neutrons) or fragments. **[13]**

The spallation process that take place in the stratosphere is:

$$^{38}_{18}\mathrm{Ar} + {}^{1}_{0}n \rightarrow {}^{22}_{11}Na + {}^{14}_{7}N + 3\ {}^{1}_{0}n$$

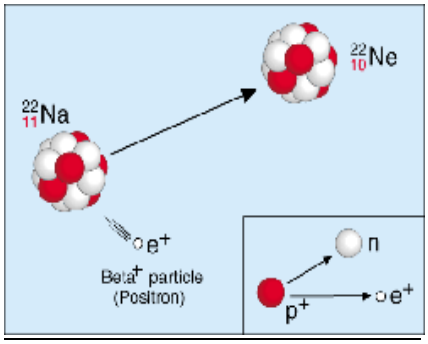
The spallation process breaks the molecule of argon into one molecule of sodium and another of nitrogen and liberates 3 neutrons, this relation could change because the nitrogen daughter could be either ^{14}N, ^{15}N or ^{16}N, thus two last are liberating only two or one neutron, the first two are stables isotopes but not the third.

- Sodium 22:

$$^{22}_{11}Na_{11}$$

The ^{22}Na disintegrates predominantly (90,4%) by β^+ decay to an excited state of ^{22}Ne. The ground state of ^{22}Ne is reached after 5,24 ps by emission of a 1274 keV photon. Competitive processes with lower probabilities are electron capture (EC: 9,5 %) and direct transition to the ^{22}Ne ground state (0,1 %). ^{22}Na has a half-life or λ of 2,6029 years. **[11]**

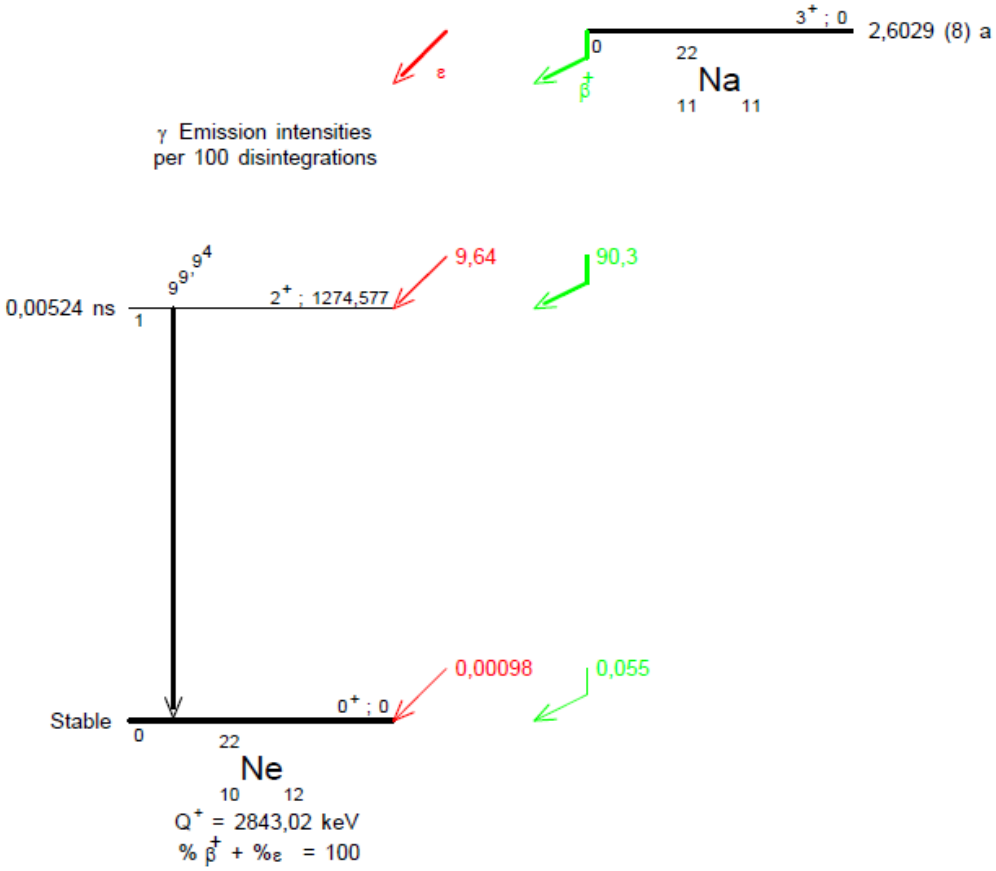
Image and equation of β^+ decay for ^{22}Na:



$$^{22}_{11}Na \rightarrow {}^{22}_{10}Ne^{*} + e^{+} + \nu_e$$

Figure 2. Decay of ^{22}Na.

*Diagram 1 with information about the disintegration of ^{22}Na. Source **[12]***



To summarize the main emissions of ^{22}Na are presented in the following table:

Table 1 with information about the main emissions of ^{22}Na.

Main emissions				
	Gamma		Beta	
	E (keV)	%	E (keV)	%
E1	511	181	546	90
E2	1275	100		

3.4. Sunspots

Sunspots are actually regions of the solar surface where the magnetic field of the Sun becomes concentrated over 1000-fold. Scientists still do not know how it happens. Magnetic fields produce pressure and this pressure can cause gas inside the sunspot to be in balance with the gas outside the sunspot but at a lower temperature. Sunspots are actually several thousand degrees cooler than the 5770 K surface of the Sun, and contain gases at temperatures between 3000 and 4000 K.

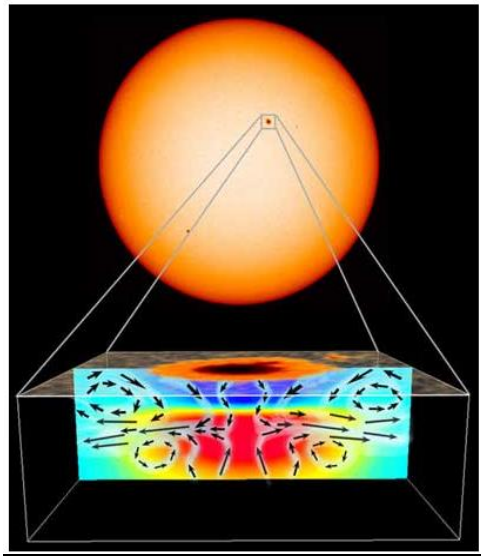


Figure 3. Sunspot with a diagram of circulation of fluxes

Sunspots affect the amout of radiation that arrives to the Earths surface, then it is possible to determine the relation between the number of points on the sun's surface and the production of ^{22}Na. Thanks to the information about sunspots from NASA we can check that relation (see setails in section 5.2). NASA was recopilating information about sunspots from 1750 and they started to have a complete information about it from 1800, but we will check them up from 2001 to 2015 because correspond to the avaliable ^{22}Na concentrations at the INTE-UPC in Barcelona. **[19]**

3.5. Aerosols

The aerosols particles in the atmosphere are liquid or solid particles. Their sizes range from a fraction of micron to several hundreds of micron (μm). Various names, such as Aitken nuclei, smokes, haze and dusts have been used in the nomenclature of atmospheric aerosols.

All aerosol particles are formed by condensation of gases or vapour or by mechanical processes such which are necessary in order to make a chain that will grow and will adopt multiples random forms. The residence times of aerosol particles in the atmosphere vary from some days near to the earth's surface in the troposphere to a year or more in the stratosphere. Atmospheric aerosols are a mixture of gases and particles that exhibit some stability in a gravitational field.

When a common aerosol is mixed with radioactive particles such ^{22}Na, ^{7}Be, ^{216}Po, ^{210}Pb and another radionuclides then the aerosol become radioactive and is possible to detect from the atmospheric air when these ones fall at ground level from upper layers in the atmosphere where these aerosols are created. The radioactive aerosols have similar physicochemical

behaviour than stable ones excepting for this added particle that makes them radioactive. **[16]**

3.6. The muons

Muons are fundamental subatomic particles, 207 heavier than an electron. Accelerators and cosmic-ray collisions produce muons but these particles quickly decay, they have a half-life of 2,2 μs. That makes muons rare in nature. The mass of the muons has traditionally been compared to the mass of the electron, in spite of the extraordinarily large difference of their masses. The relation between them is expressed by the empirical formula:

$$m((\mu) = \mathrm{m(e)}(1 + 3/2\alpha) = 206{,}554\ \mathrm{m(e)} = 105{,}658\ \mathrm{MeV}/c^2 \quad (2)$$

Where μ symbolizes the muon and *e* the electron and α came from the theory of special relativity to the dilatation of time. **[17]**

3.7. The chemistry of ^{22}Na

The Sodium is an element which is a member of the alkali metal group with symbol [Na]. It is physically silver coloured and a soft metal of low density. Pure sodium is not found naturally on earth because it is a highly reactive metal. The sodium ion is abundantly found within the Earth's oceans, bodies of water, and many minerals. It is used for chemical synthesis, analysis, and heat transfer applications. Sodium is also a crucial element for animal and plant life by creating charge gradients and assisting in the development of energy.

Sodium reacts exothermically with water, releasing heat when it contacts with water by the chemical reaction:

$$2Na_{(S)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)} \quad (3)$$

The electronic configuration of sodium's shell is: [Ne] $3s^1$, it means that sodium has two electronic shells complete with electrons at the corresponding energy from the electronic band structure and then remains one electron at the third shell which is really easy to take from another polarized molecule such, water, chlorine, fluorine, nitrogen and many more.

When ^{22}Na is in the air and it starts to rain, then happens the reaction (2) and water absorbs all the sodium in the air including ^{22}Na because it has a free energy of: $\Delta G_f^0 = -419{,}2\ \left(\frac{KJ}{mol}\right)$ which is really lower than 0, it explains why it is highly reactive with water. **[18]**

3.8. Previous information about ^{22}Na available in the literature

This graphic has been taken directly from the work of Bhandari et al **[1].** It is very important

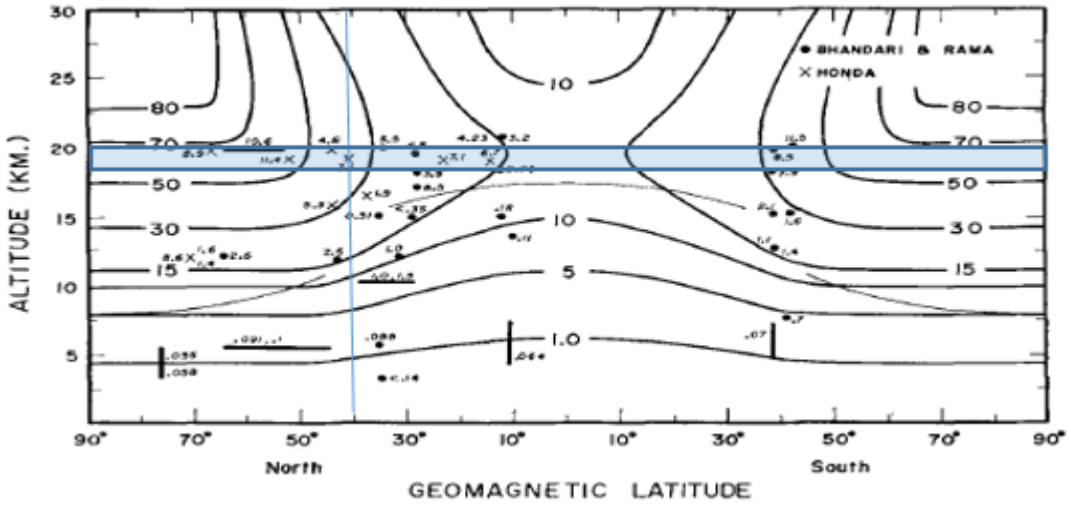


Figure 4. Graphic of altitude vs geomagnetic latitude. Used unit d.p.m. Solid lines represent equal concentration of ^{22}Na and the thinest line represents the tropopase. Source [1]

what the graphic shows and the conclusions that can provide us because describe the ^{22}Na dependence with altitude and latitude (our geomagnetic latitude is ~41ºN and it is marked with blue colour in a vertical line). The blue band marks where the tropopause at our geomagnetic latitude is (usually between 18 and 20 km high). The conclusions from this study related to this project are:

- The maximum production of ^{22}Na happens at the tropopause where also accumulates and reaches maximum activity of this radionuclide.
- Practically there is no production at the sea-level so all what is detected come mainly from the tropopause.
- High production of ^{22}Na at high latitudes, low production at lower latitudes.

According to Blazej et al, the ^{22}Na has a seasonal activity at the ground-level, fact that we will have to check if it is true or not in our location. **[2]**

Długosz-Lisiecka et al pointed out that cosmic radiation interacts with O_2, N_2 and another components which exist in the atmospheric air producing radionuclides. The aerosols have a residence time similar having nuclides of ^{22}Na or ^{7}Be (there are many kinds of aerosols). **[3]**

According to the work of H. Tokuyama and S. Igarashi, the nuclear tests from 1960 to 1962 increased the level of ^{22}Na, in Fukui City, Japan. Nearby there were nuclear facilities in which the reactor used ^{23}Na (the stable isotope of sodium) as a refrigerant which reacts with the

neutrons from the core of the reactor and transform ^{23}Na into ^{22}Na liberating two neutrons. Sometimes this reactor released a little portion of this refrigerant to the atmosphere, this portion increased the levels of ^{22}Na in Fukui City. From this article, the most important to highlight is that exists also ^{22}Na that is produced in artificial way and it is possible to measure it. Also the precipitation affects to the concentration because the rain takes the aerosol from air and as liquid state drops to the soil. **[4]**

According to the work of Grabowska et al the concentration of ^{22}Na depends on the solar cycle, as higher is the solar activity, higher is the production of ^{22}Na because the sun emits more photons that arrive to the atmosphere, this cycle lasts approximately 22 years. **[5]**

Jasiulionis et al, also studied the ratio of production of ^{22}Na in function of the number of photons that arrive to the atmosphere, approximately 32.258 photons are needed for that will be produced a single radionuclide of ^{22}Na. **[6]**

The article from Lepanen et al **[7]**, describes the transforming process from cosmogenic photons until the production of ^{22}Na, it explains what happens with this process and give the information of the spallation process that takes place, this process happens at neutrons energies of 200 MeV and needs much higher energy than the reaction with O_2 (about 20 MeV) what means that it is easier to make radionuclide from oxygen than from argon and also explain the difference of concentration from nuclides that comes from Ar or O_2.

Steiner et al **[8]** described a method to determine the cosmogenic ^{7}Be and ^{22}Na in Switzerland, and also quantified the ^{22}Na produced by Fukushima with a limit of detection of 0,25 $\mu Bq/m^3$.

4. Instrumentation and methodology

4.1. Location

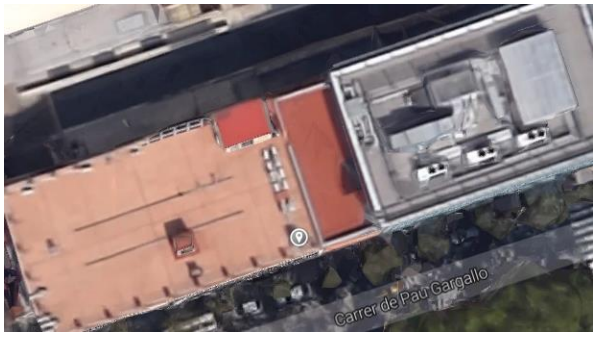


Figure 5.The roof from the INTE facilities

Samples of air aerosols are collected weekly at the permises of the INTE-UPC, located in Barcelona with a high-volume dust sampler located on the roof of the C building at the ETSEIB (School of industrial engineering of Barcelona), located exactly at 41º23'2'' N, 2º6'58''E, at 66 meters above sea level [This information has been provided by Google maps].

The point that is marked in this picture is the location of the high-volume sampler.

4.2. Climatic characteristics

The climatic characteristic of the region is imperatively important to be able to predict the behaviour of ^{22}Na. When it rains the ^{22}Na reacts with the falling water as it is explained in the section (3.7) and sticks to the soil as NaOH and practically disappears from the atmospheric air in the region where rains.

We are in a humid Mediterranean climate and the irregularity in the intensity and times that precipitates is typical for this area of Barcelona. With those information it is easy to predict that will have many irregularities in ^{22}Na concentrations because rain cleans up the atmospheric air. Typically in Barcelona the temperature oscillates between ~0 ºC to ~40 ºC. The temperature will affect the concentration at ground level of ^{22}Na, because it helps to accelerate the exchange of air masses between the stratosphere (where ^{22}Na is generated) and the ground level air.

4.3. Description of a coaxial detector of Germanium

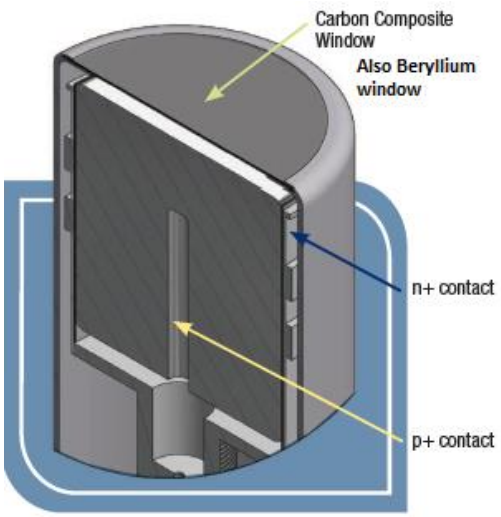


Figure 6. Schematic view of a Ge dectector.

The CANBERRA XtRa is a coaxial germanium detector having a unique thin-window contact on the front surface which extends the useful energy range down to 3 keV. Conventional coaxial detector has a lithium-diffused contact typically between 0,5 and 1,5 mm thick. This dead layer stops most photons below 40 keV or so rendering the detector virtually worthless at low energies. The XtRa detector, with its exclusive thin entrance window and with a Carbon Composite cryostat window, offers all the advantages of conventional standard coaxial detectors such as high efficiency, good resolution and moderate cost along with the energy response of the more expensive Reverse Electrode Ge (REGe) detector. The effective window thickness can be determined experimentally by comparing the intensities of the 22 keV and 88 keV peaks from ^{109}Cd. With the standard 0,6 mm Carbon Composite window, the XtRa detector is guaranteed to give a 22 to 88 keV intensity ratio of greater than 20:1. **[20]**

Table 1. Shows the characteristics of the germanium detectors avaliable at the LARA INTE-UPC

Given name	Ge-3	Ge-4	Ge-5
Type	Coaxial inverted, n-type.	Coaxial window of cryostat of beryllium, p-type.	Coaxial window of cryostat epoxide of carbonium, p-type.
Model	GR2020	GX3020	GX4020
Cristal volume of Ge (cm^3)	98	137	171
Primary shield	Lead (10 cm)	Steel (14,4 cm)	Lead (10,5 cm)
Secondary shield	Copper (2 mm)	-	Copper (2 mm)
Relative efficiency	23,2 %	33 %	40,9 %

In this report the main used detector was a coaxial detector with a carbon cryostat window

(Ge-5) p-type, because it is the most efficient detector available at LARA INTE-UPC since it was required the maximum efficiency possible in order to obtain the lowest possible uncertainty.

4.3.1. **Overview of the detectors in the laboratory**

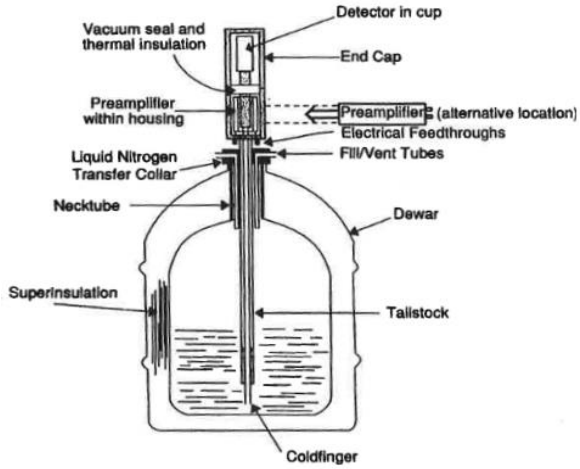


Figure 7. Schema of germanium detector

Figure 8. Detector Ge-5

In the figure 7, we can observe the typical germanium detector with the Dewar reservoir and the location of electronical components such the preamplifier and another.

The bottom of the reservoir of nitrogen is connected with the coldfinger to the detector, which provides a constant temperature to the detector. This liquid nitrogen is at atmospheric pressure so it boils at 77 K, all the nitrogen is boiling into the Dewar and that is why it maintains constant temperature. This Dewar has a capacity of 30 L and every week it has to be refuelled in order to keep the level of liquid nitrogen constant and it will keep going into the coldfinger, when nitrogen rises the detector it is liberated as gas of nitrogen reducing the probability to make wet any surface into the detector. In order to avoid unexpected condensation of water due this cold temperature, all the detector must be really clean and without humidity, this is why the laboratory has a controlled temperature and humidity.

4.3.2. Semiconductor as a radiation detector

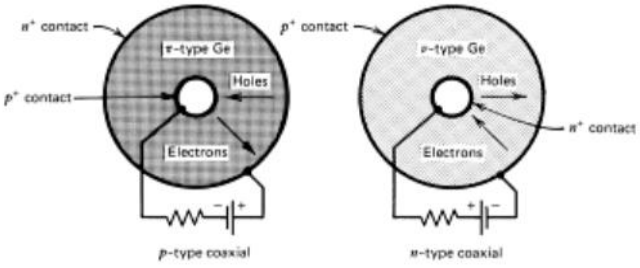


Figure 9. Carrier lines inside the semiconductors p-type and n-type.

In order to make the semiconductor more efficient the external and internal surfaces have been doped with impurities of the chemical groups 3 and 5 from the periodic table of elements, in order to create free ions that will give a larger electrical current. The elements from the group 3 are called impurities of p-type and they generate holes in the valence band generating a positive charge of the atom creating a cation in elements such barium, aluminium, gallium and another doping the germanium. The elements from the group 5 are called impurities of n-type they give one electron to the conduction band and this generates one anion in elements such nitrogen, phosphor, arsenic and another elements from this group.

In the crystal of germanium of the detector number 3 the external contact is done with an n-type of impurities and in hole inside is p-type. Crystals from detectors number 4 and 5 are inverse to number 3 is outside with impurities p-type and inside n-type.

Germanium is used as detector because is the semiconductor with the lowest band gap. That means with weak energies you can ionize an atom of Ge it is needed just 0,66 eV or more in order to create a pair hole-electron (at the temperature of 300 K, at 77 K more energy is required) and this will create an electric current and this current will be detected. This kind of detectors needs to operate in cold conditions at temperatures of 77 K, normally they are refrigerate with N_2 liquid in order to avoid electronic noise.

4.4. Packaging of Detectors

The detector is mounted within a thin aluminium retaining sleeve which also forms an outer contact with the detector. The core contact is made either with a conical pin or a spring loaded pin extending within the hollow core. The whole of this arrangement is fixed to a pedestal which is in turn fixed to the cooper cold finger which extends through the whole cryostat to the liquid nitrogen reservoir. The complete assembly is covered by the end cap to form a sealed chamber. The upper part of the detector housing is evacuated and thermally insulated from the rest of the housing. A pack of charcoal or molecular sieve absorbent will be mounted in the detector chamber to absorb traces of gases left after evacuation when the detector is cooled.

Beneath the detector pedestal are secured the preamplifier FETs (flied effect transistors) which need to be cooled in order to do not transfer electrons from the valence band to the conduction band by the temperature of the semiconductor in this case Germanium. If that effect happen it would make false counts because the electrons would have energy enough for jumping the energy gap (from the model of bands that is included in the quantic theory) and create a count. This differential of potential is too low as for be counted in digital technology so it need an pre amplifier in the cryostat that will not increase the temperature inside (saving liquid nitrogen in order to refrigerate that) and the signal it is enough strong as for arriving to the amplifier outside the shelter.

Then the signal from the preamplifier arrive to the amplifier, is translated to a digital signal that can be processed by the multichannel analyser and then processed by the program Genie2000.

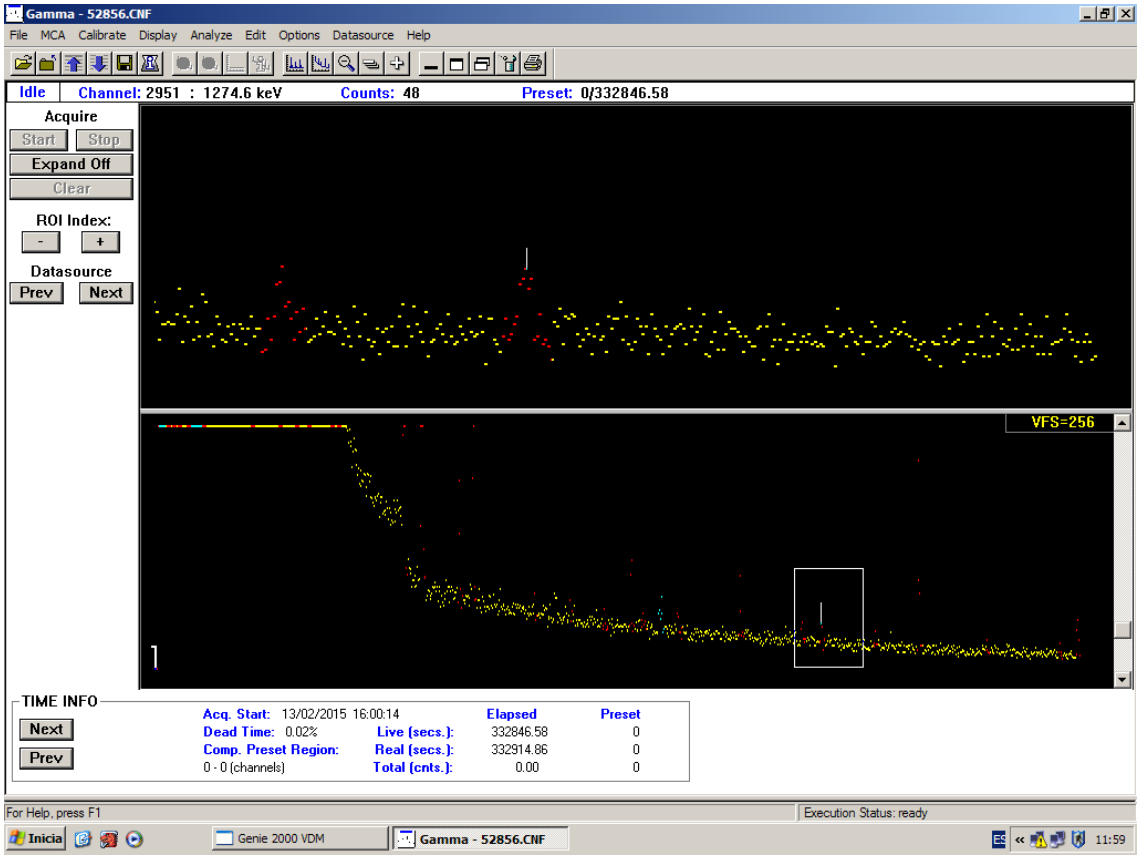


Figure 10, example of an spectra from a filter. At the upper part is the amplified those points near to ^{22}Na energy. The peak of ^{22}Na is pointed with a vertical gery line.

4.5. Genie2000

The Genie 2000 is a software used at the LARA INTE-UPC in combination with the equipment of the detector provided by Canberra Industries in order to determine the activity of determined isotopes and provide their MDA, their energy peak and another relevant parameters.

The management of the data taken from the multichannel is carried out with this software Genie2000. It also allows the definition of libraries for the different isotopes in order to be analysed either in a qualitative and quantitative way.

The parameters that will be needed for our analysis will be described:

- Currie MDA (minimum detectable activity): In this algorithm, the detection limit (L_D) is calculated using:

  $$L_D = k^2 + 2 \cdot L_c \quad (5)$$

  From equation (5) the last parameter to define is defined as:

  $$L_C = 2 \cdot k \cdot \sqrt{\frac{T_S}{T_B} S_B} \quad (6)$$

  From equation (5 and 6) we have that *k* comes from the confidence levels (α and β) and *k* values of a Poisson distribution.
  S_B is the peak area of the equivalent peak in the background spectrum.
  T_S is the live time of the spectrum.
  T_B is the live time of the background spectrum.

  Which is then translated into MDA using the following equation:

  $$MDA = \frac{L_D}{T_1 \cdot \varepsilon \cdot y \cdot V \cdot K_C \cdot K_W \cdot K_X} \quad (7)$$

  Where

  ε is the attenuation corrected efficiency.
  y is the branching ratio of the gamma emission under consideration.
  V is the volume of the sample.
  K_c is the correction factor for the nuclide decay during counting. Equation (9).
  K_w is the correction factor for the nuclide decay from the time the sample was obtained to the start of the measurement. Equation (10).
  K_x is the correction factor for decay during the sample accumulation for air filters. Equation (11).

$$T_1 = T_C \cdot T_W \cdot T_X \quad (8)$$

Where

T_C is the elapsed time real clock time for the counting.

T_W is the elapsed time, real clock time the sample was collected and the start of the measurement.

T_X is the sampling period.

Notice that all the times must be in the same units.

$$K_C = \frac{T_{1/2}}{\ln(2)\cdot T_C} \cdot \left(1 - e^{-\frac{\ln(2)\cdot T_C}{T_{1/2}}}\right) \quad (9)$$

Where $T_{1/2}$ is the half-life of the radionuclide that is being studied.

$$K_W = e^{-\frac{\ln(2)\cdot T_W}{T_{1/2}}} \quad (10)$$

$$K_X = e^{-\frac{\ln(2)\cdot T_X}{T_{1/2}}} \quad (11)$$

With all this previous information we obtain a single equation for the Currie MDA, which will be used in order to realize calculus about the minimum of detectable activity.

- The efficiency of the ^{22}Na (1274,577 keV) that we used in chapter 6 can be expressed as follows:

$$\varepsilon = \frac{A}{T\cdot 60\cdot I_0 \cdot e^{-\lambda\cdot t}} \quad (12)$$

Where

A net area of the photopeak in counts of a ^{22}Na standard.

T is the T_1 but for the standard.

I_0 the initial activity of the standard (38,1 KBq).

t the decay time of the standard in years.

λ is the half-life of the ^{22}Na in years (2,6029 years)

All the information of this section have been taken from the bibliographic reference **[22]**.

4.6. Radioprotections in LARA's laboratory

The laboratory detection room is a room where is possible to measure really low concentrations of radionuclides because it has a special protection from the natural radiological background.

This protection consists in an oversized 1 meter wall of concrete and with concrete that has a really low content in radioactivity. The air supplied to the detection room is previously filtered with an activated carbon filter to remove the radon and all the aerosols from outside, the temperature and humidity of the room are continuously monitored.

4.7. High-volume sampler

Figure 11. The captor station of radioactive aerosols of high volume.

The captor station of radioactive aerosols of high volume is the model ASS-500 developed by the Central Laboratory for Radiological Protection (CLOR) of Warsaw. This unit has a pump flow of about 700 m^3/h, it means that weekly it can pump between 80.000 m^3 and 100.000 m^3.

This machine has many instruments in order to measure with a high precision the air flow, it also has a counter that is possible to reset in order to count air volume that passed through the pump. At the top of the machine is placed a resistance that makes light and radiates with infrared light the filter in order to keep out the water and avoid at maximum the water into the filter.

The flow that pass through this pump is in all it area at the same speed, it has been designed in such way that the filters will have a homogeneous concentration of aerosols.

4.8. Filters used for capture the aerosols with radionuclides

The filters are made of polypropylene G3 with a surface of 44 x 44 cm^2 but the active surface is of 42 x 42 cm^2 with a total surface of 1764 cm^2 with a surface density of 140 g/m^2. These filters are used for capture the radionuclides with an efficiency between 93 and 99 %. This filters are placed into a framework which fits exactly into the capture unit, for this reason the filters lose 1 cm on each side.

Fresh filters have originally a weight of 27 g, after the capture of aerosols, dust, pollen, water and another little particles form the air, and they can weight over 33 g at the end of the sampling period.

They have to be into an oven at 105 ºC during 1 hour in order to take of all the remaining humidity from the filter and make the correct measure of weight to measure its activity.

4.9. How the available spectrums were analysed

This process can be characterized with 3 steps:

1) Acquisition of information about filters that LARA collected weekly since 2001 and where they are located. There is basic information about almost 800 filters that we have to reanalyse. As it has been already mentioned ^{22}Na is not usually reported and thus spectra from these filters have to be reanalysed to report ^{22}Na concentration. This information relative to filters includes: the number of the filter, the reference number of the filter, the number of the electronic file inside the program Genie2000, and the identification of the detectors that have been used to analyse them.
2) Assess the background correction. Natural background should be subtracts to determine the correspondent activity of the isotopes of interest.
3) Reanalyse the spectrums with Genie2000.
4) Stack all the information about ^{22}Na, such activity, MDA or uncertainty of the results and analysis with Excel.

All this process required a little more than 2 weeks due to the quantity of spectra ~800 filters which required each one of a few minutes for complete this steps. They were done in the most efficient way possible for analyse them as much fast was possible without make a mistake.

4.10. Calibration of gamma detector

In order to quantify the activity of the radionuclides it is necessary to calibrate the detector, at a qualitative level (calibration of energies: channel-energy) and at a quantitative level (calibration of efficiencies: energy-efficiency).

To calibrate the system a radioactive standard is needed, commonly is a mixture in aqueous solution of gamma emitters with different energies and concentrations, and is certified. It is necessary to ensure that the radioactive standard cover all the range of energies that we are going to study.

From this certified standard solution it is necessary to prepare a diluted standard solution with a known concentration and prepare a standard with exactly the same geometry than samples of interest. It is usual to use the same source for calibrating the energies and the efficiencies.

4.10.1. How has been prepared the standard geometry

A standard was set-up using a certified solution from Amersham International that contained:

^{241}Am, ^{57}Co, ^{109}Cd, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{90}Y, ^{60}Co

These radioisotopes provide us a spectra with peaks conveniently distributed in a wide range of energies from 59,5 keV up to 1826 keV. (In this peaks the sum effect it is negligible (Gilmore and Hemingway, 1996)). A filter was spiked with this mixed gamma ray standard, the filter was folded and pressed to obtain a final size of 8x8 cm^2 and it was packed in a box of 10x10x2 cm^3.

Figure 12. Standard filter for calibrating the gamma spectrophotometer.

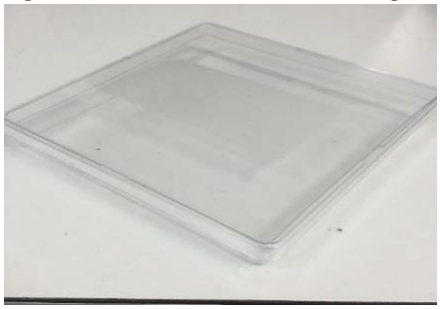


Figure 13. Container.

Figure 14. container with a fresh filter.

Figure 15. Detector 5 (GE-5) internal view .

Here we can observe the filter that has been spiked with drops of the cocktail, one by each intersection.

The first from the left is a general view of the filter at the right side, is the pattern with a few drops of standard in the filter, at figure 13 it is the container.

Then we have a general view of a fresh filter inside the container its final configuration ready for going to the detector (figure 14).

In the figure 15. At the right side is placed a tube that conects the can of the nitrogen. Also is possible to appreciate the 2 mm layer of cooper and part of the lead of the 10 cm thick-shield.

The mean full energy peak efficiency was calculated as function of gamma-ray energy using Genie2000 and a logarithmic polynomial fit was established. Two regions were used, for the low-energy range (up to 122 keV), and another for the high-energy range (up to 1826 keV).

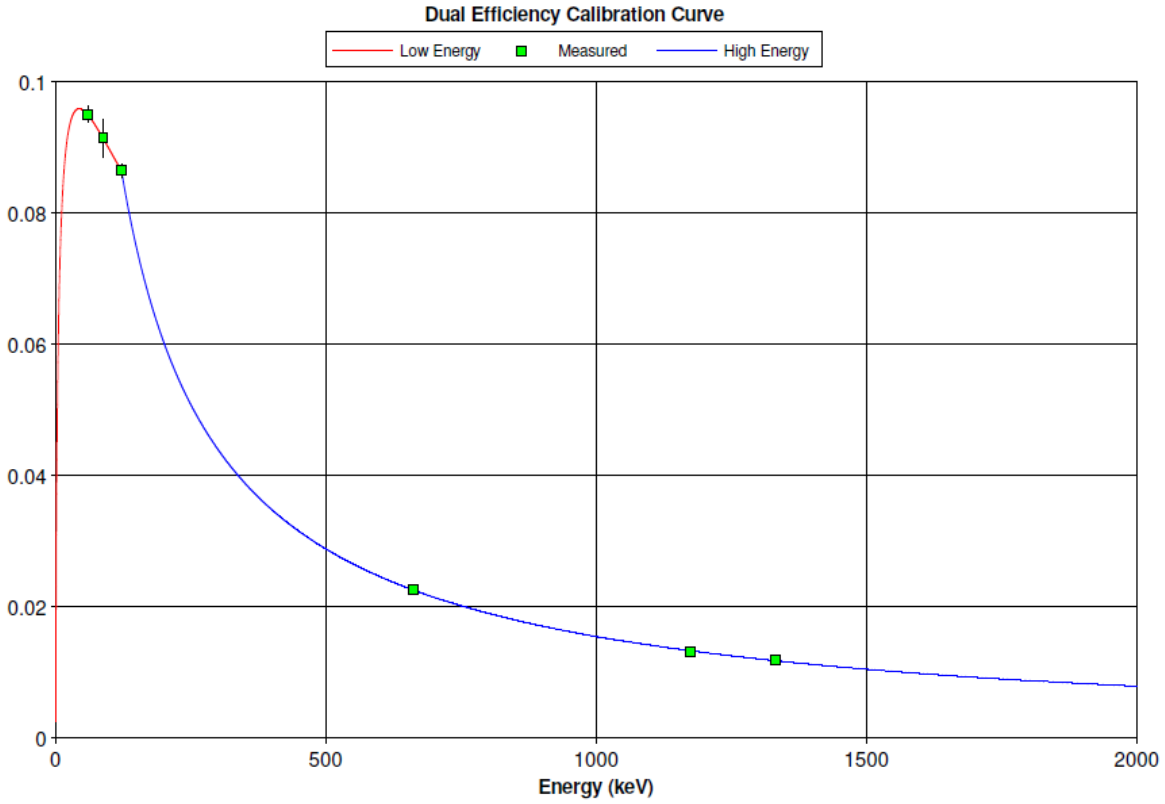


Figure 16. Graphic between the energy and the efficiency of the detection for the calibration of the detector 5.

This graphic has two different regions, of high energy and of low energy with a regression equation:

High energy: $\ln(Eff) = -3{,}785 + 0{,}7479 \cdot \ln(E) - 0{,}09895 \cdot \ln(E)^2$

Low energy: $\ln(Eff) = -0{,}3894 - 0{,}0157 \cdot \ln(E) - 0{,}05647 \cdot \ln(E)^2$

Then at the energy of Na^{22} of 1274,577 keV with the regression equation for high energy we obtain a theoretical efficiency equal to 1,19 %.

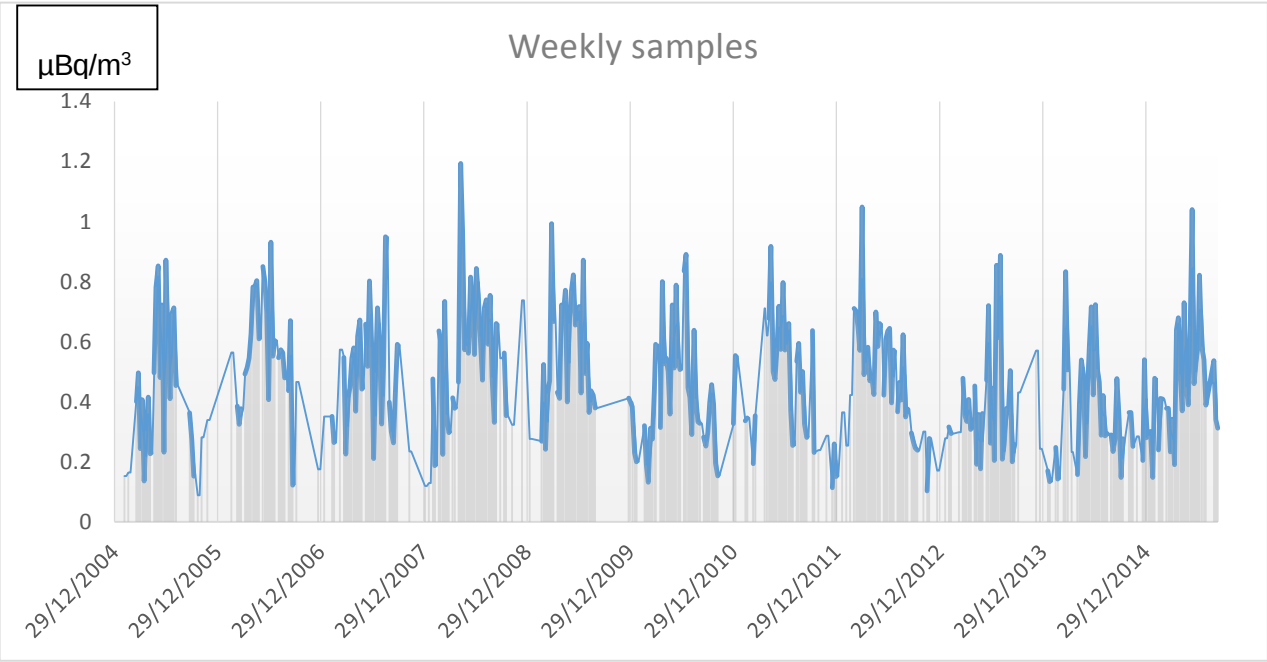
5. Report of the results

In this part we are going to focus on determine the concentration of ^{22}Na during the years 2005 to 2015 with details. Previous to 2005 the information was not enough as for being able as to assess well ^{22}Na concentration in air because the program and methodology did not allow to do it. For those filters obtained before 2005, nowadays is impossible to measure again their concentration of ^{22}Na because it almost fully decayed after 5 or 6 times the half-life (2,6 years approximately) and even in the best case could not be enough as for detecting it nowadays.

In this part also we are going to show all the studied variables that affect the concentration of ^{22}Na and its statistical relations.

5.1. Concentration of ^{22}Na during period 2001-2015

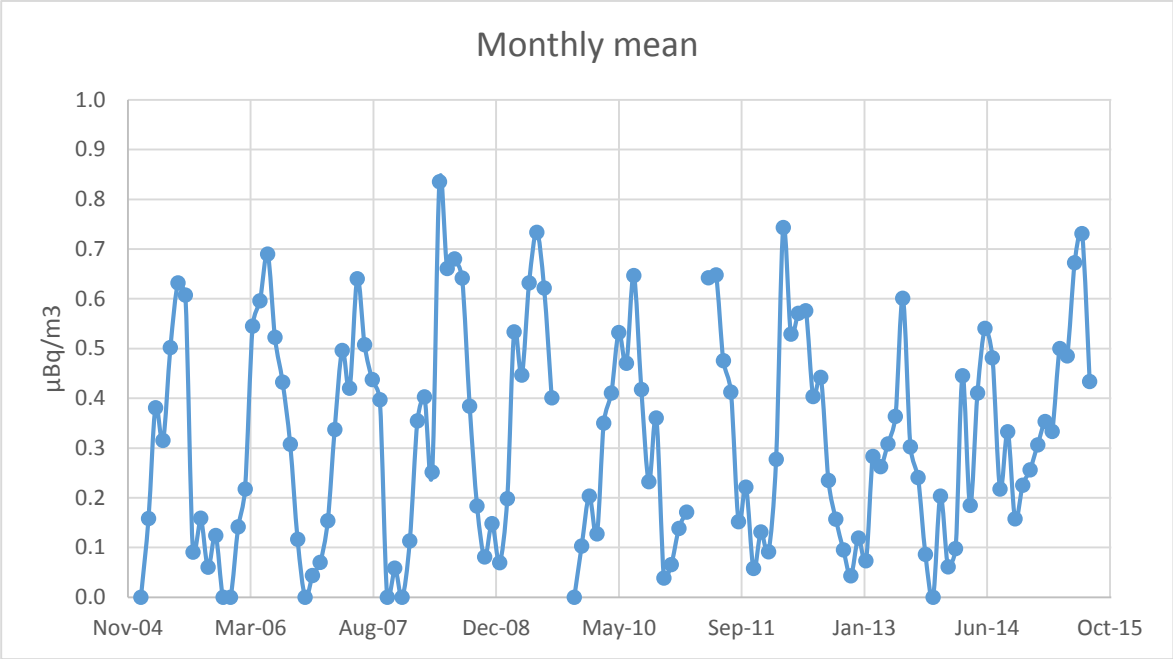
From the 800 filters analysed with a confidence level of 95 % we obtained a graphic in function of time (weakly samples):



Graphic 1. Concentration of ^{22}Na versus time.

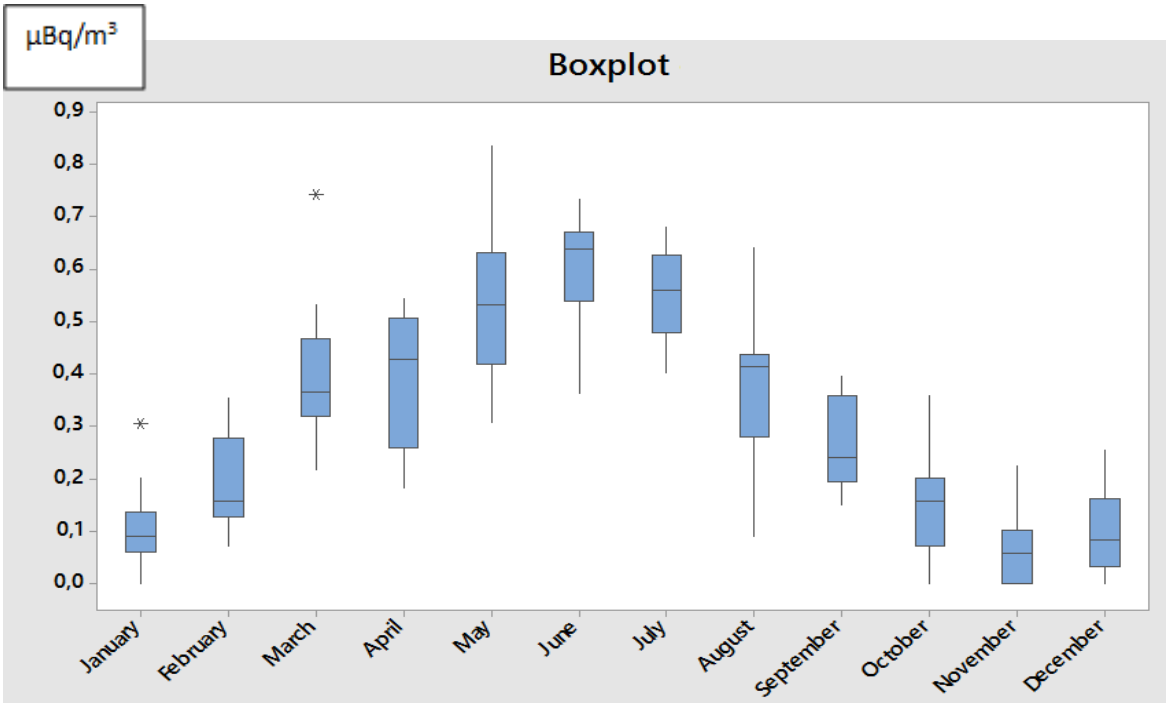
First 227 filters were not possible to graphicate so are not included in this graphic.

In order to analyse the information contained in graphic number 1, we are going to show the monthly mean values and also the boxplot by months and by season to confirm the seasonality of the concentration of ^{22}Na at the ground level.



Graphic 2. Montly mean value of ^{22}Na versus time.

From graphic 2 we can clearly deduce that it has an increase in its concentrations during the warm seasons of the year and present really low concentrations during cold seasons.

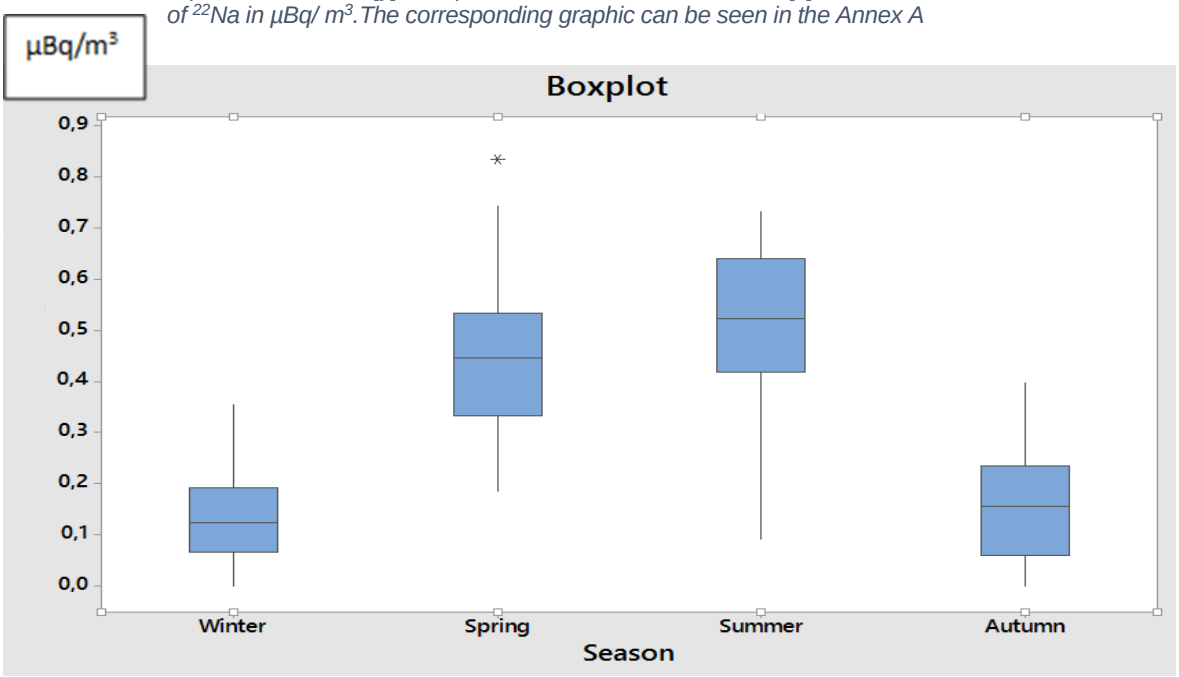


Graphic 3. Boxplot of the mean of all the months in the analysed period. In units of µBq/m^3

The graphic number 3 confirms that the concentration of ^{22}Na is seasonal and in warm months the concentration rises up to the maximum, during this period mostly in June is where it can be observed the maximum of the concentration of ^{22}Na, but in a few cases in May. In November ^{22}Na shows its minimum concentration, and sometimes it is not possible even to detect the presence of ^{22}Na. Then to predict how it behaves we made a regression of 4 degree because of trial - 3rd and 5th and first one did not adjust well enough and then we tried also 5th degree but the gain was of 0,01 in the R^2 so we conclude 4th degree is the most efficient for correlating the activity of ^{22}Na we have an R^2=0,9758 and the equation is the next one:

$$y = 0{,}0007 \cdot x^4 - 0{,}016 \cdot x^3 + 0{,}1048 \cdot x^2 - 0{,}1199 \cdot x + 0{,}1168$$

Equation 13. Where [y] it's equal to the number of months and [x] is the concentration of ^{22}Na in µBq/ m^3.The corresponding graphic can be seen in the Annex A



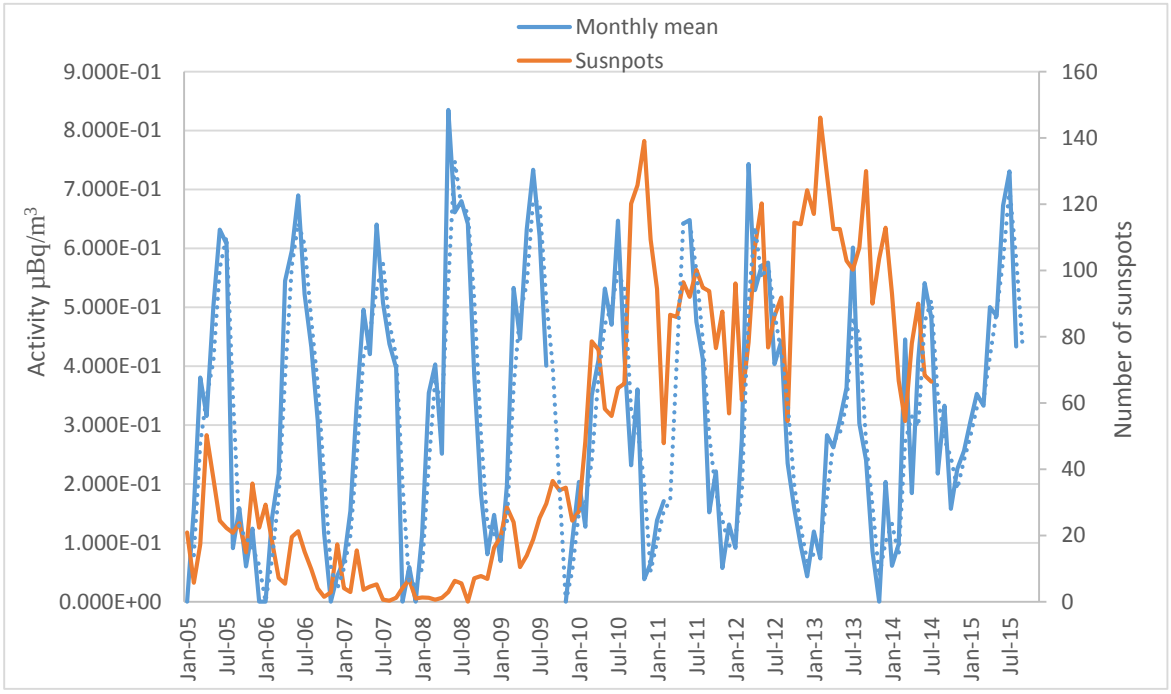
Graphic 4. Boxplot of the mean of all the months in µBq/m^3 and distributed by seasons in the analysed period. Have been considered months of winter: December, January and february, months of spring: March, April and May, months of summer: June, July and August and months of autumn: September, October and November.

With this boxplot we can see that in summer ^{22}Na has greater activities than in any other season, but in spring when temperatures rise up, ^{22}Na shows also high concentrations.

5.2. Relation with sunspots

This relation had to be weak because most part of particles that could make a spallation with argon are blocked by the magnetosphere (exactly 98 % of this particles), the other 2 % could start the spallation process in order to generate ^{22}Na, and from this 2 % only a fraction will impact with an atom of argon. As it is easy to predict, the production of ^{22}Na that can generate the radiation from sun is really limited, to make an adequate analysis of the influence of sunspots it would be required information of a whole solar cycle (22-23 years) but we only have 10 years, this is why is expected to find a weak dependence.

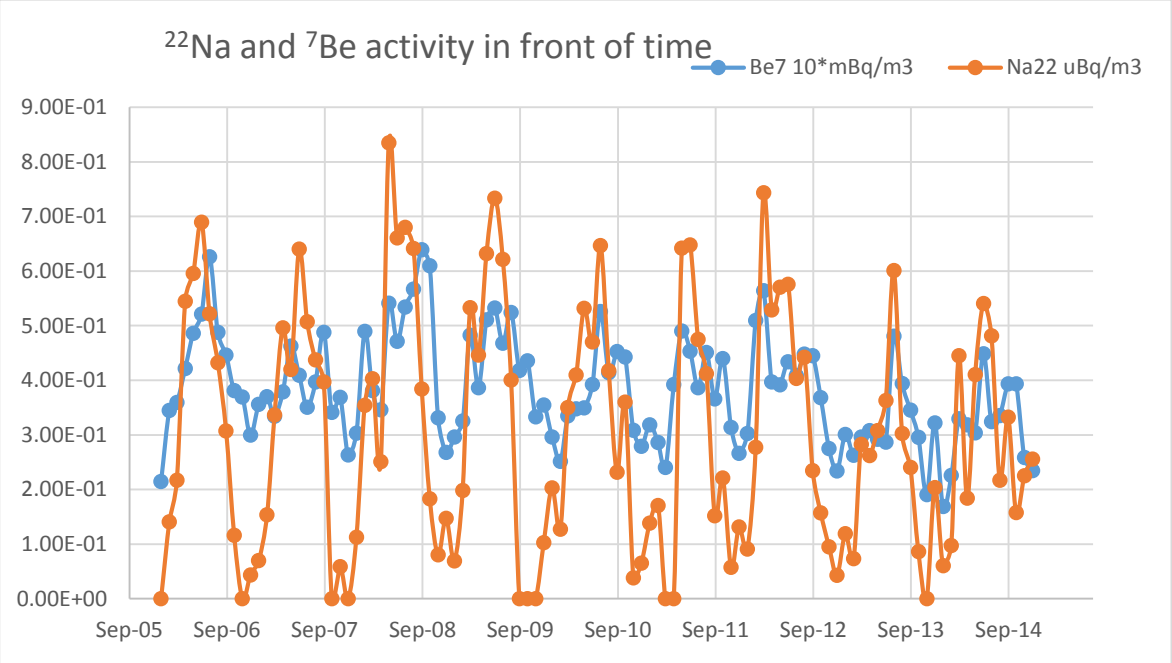
The solar activity is related with the number of sunspots on the surface of sun and NASA has the results of the monthly mean of sunspots on the surface of sun since 1750 so we used their data base in order to compare with the concentration of ^{22}Na during the specified period, and graphic 5 shows the results:



Graphic 5. Graphic of the monthly mean concentration of ^{22}Na during the period 2005-2015 and at the right side the monthly mean of the number of sunspots.

An analysis of variance of this variable, shows a p-value of 0,953 it means that it explain at 4,7 % of the relation between sunspots and the concentration of ^{22}Na at the ground level.

5.3. Comparison between activities of ^{22}Na and ^{7}Be



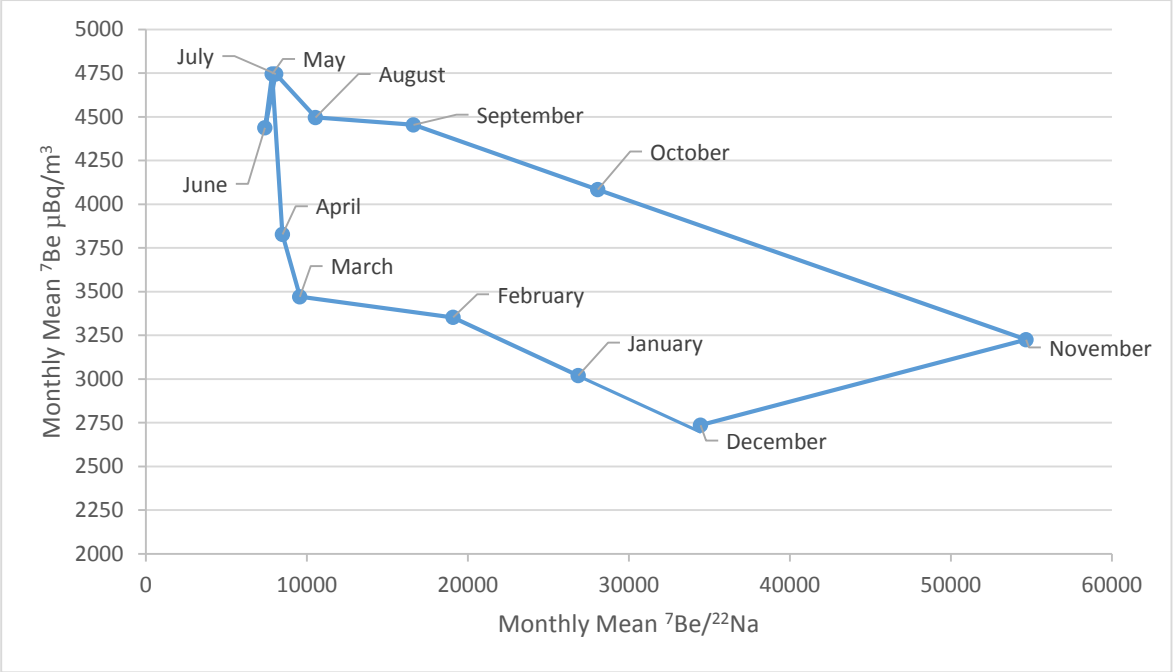
Graphic 6. Is being compared the ^{22}Na with ^{7}Be, notice that the concentrations have been escalated in order to compare their evolution during the year.

In the graphic 6 we can see perfectly that their behaviour is practically the same in general terms, during warm seasons the concentrations increase but when it is cold they decrease.

Both are cosmogenic radionuclides, they are generated by the same source (cosmic radiation), the ^{7}Be comes from a different spallation process related to nitrogen or oxygen or carbon and a neutron. As it is well-known the concentration of nitrogen plus oxygen plus carbon versus argon are quite different, the first ones are about thousand times the concentration of second one it explains the difference of concentration between ^{7}Be and ^{22}Na.

When it rains the concentration of ^{22}Na decreases dramatically because it is highly reactive with water, makes it interact and form NaOH and drop to the soil and clean up the air from this radionuclide. In the case of ^{7}Be is less reactive with water in order to form $Be(OH)_2$ this is the main reason that make that the concentration of ^{7}Be in the air does not decrease so dramatically like ^{22}Na and then in all weathers it is possible to measure it with a concentration higher that the MDA (for the ^{7}Be).

5.4. The cyclic relation between ^{22}Na and ^{7}Be



Graphic 7. ^{7}Be concentrations vs ^{7}Be/^{22}Na ratio of monthly averages of all ground level air samples.

Following the methodology of Steinman et al **[8]** the cyclic relation of ^{22}Na and ^{7}Be is showed at the graphic 7, obtaining similar results.

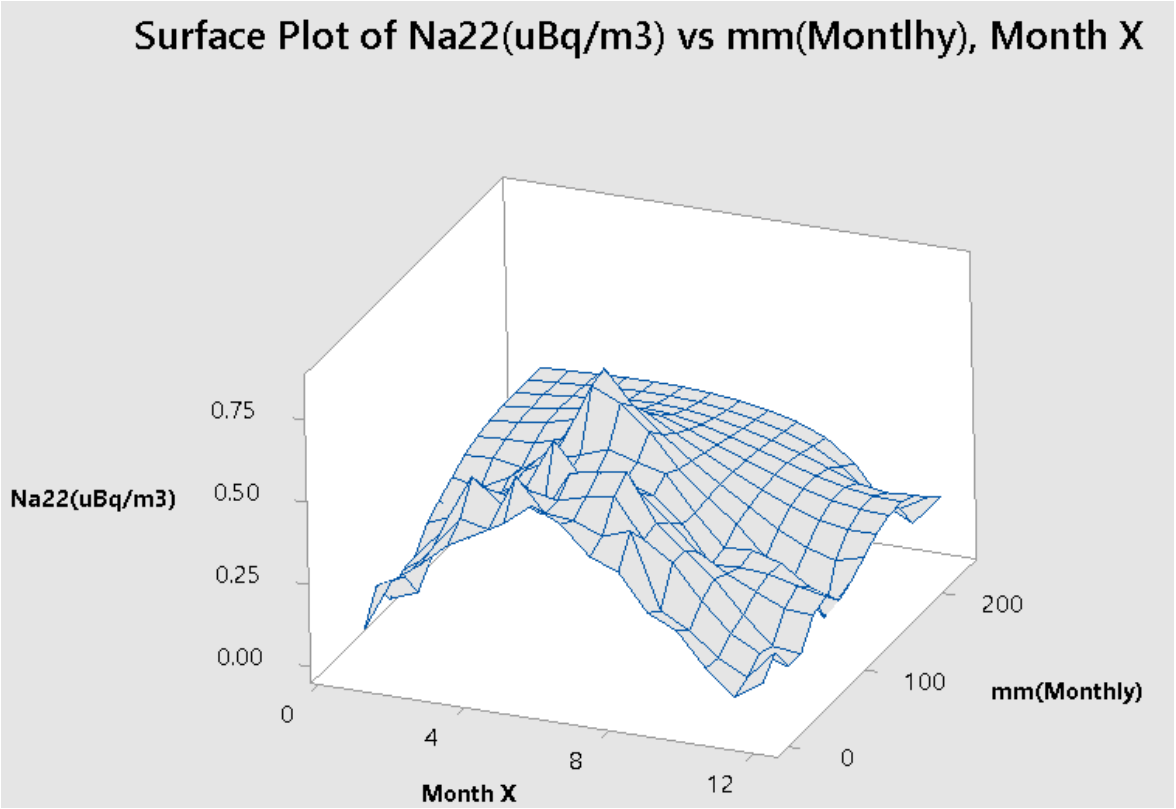
In our graphic we can also determine the 4 phases that have been also observed in the Swiss study of Steinman et al. **[8]**

- Phase A: the prominent spring input of cosmogenic isotopes from the lower stratosphere starts in March and finish in May.
- Phase B: important downward mixing upper tropospheric air, starts in May and finish in July.
- Phase C: lowering of the mixing height, it starts in August and in our case finish in November (in Swiss studies finish in October).
- Phase D: limited mixing where the concentrations of radionuclides are stratified and decayed the concentration of ^{7}Be because its short half-life.

Then we can realize that the behaviour in both cases are similar even with its geographic and all altitude differences.

5.5. Relation between rain and concentration of ^{22}Na

From all the information available on the web page *meteocat.cat* about the average monthly rain in mm/m^2 (usually called as mm in meteorological language), we have got the information from 2008 to 2014. In order to maximize the visual understanding of this information we have made a 3D plot with the months as the X axis and the monthly average concentration of ^{22}Na as Z axis leaving the mm of rain in Y axis.



Graphic 8. ^{22}Na and mm of water rain monthly averages vs month.

In the graphic 8 we can perfectly observe that the concentration of ^{22}Na, is affected also by the rain, as much more it rains there is less concentration of ^{22}Na. (In this graphic is plotted monthly averages of water rain).

This mm of water rain are not perfectly representative, because it is possible that once a month it will appear downpour rain and then, on this day it 'washes' the atmosphere from ^{22}Na but the average of all the month of ^{22}Na will not be disturbed because the other 3 weeks will correct this effect, as it happens in July when it rains 100 mm but it doesn't change with 0 or 50 mm of rain from another year.

5.6. Relation between the concentration of ^{22}Na and the temperature

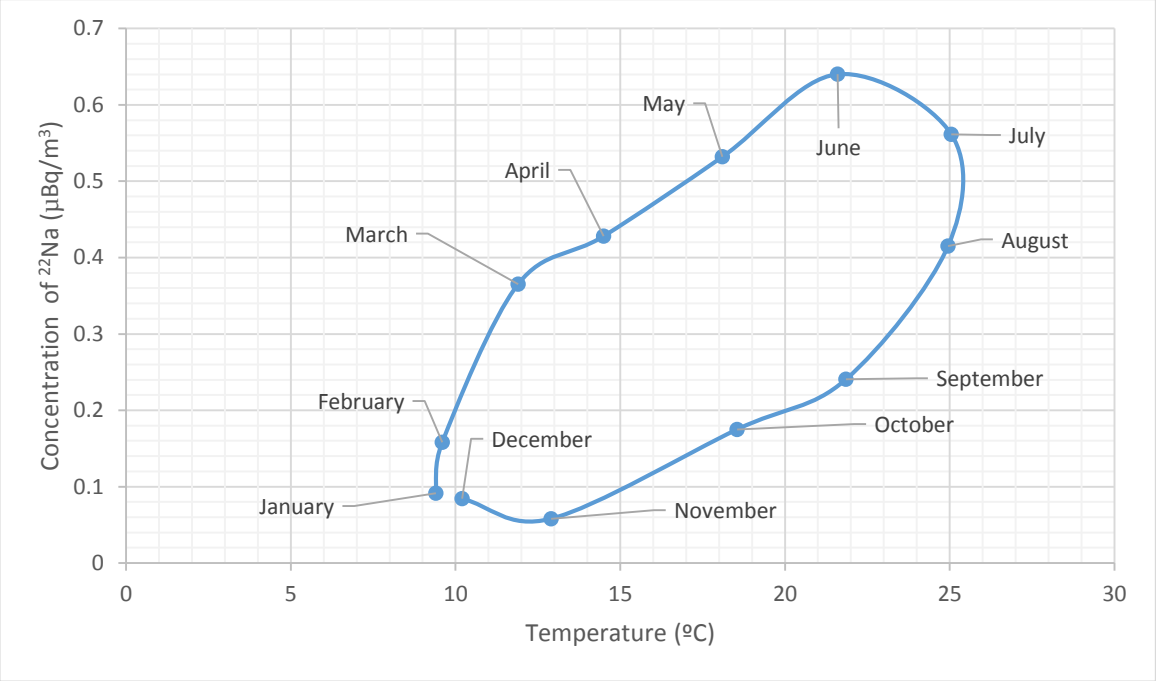
In this part we are going to show the possible relation between the temperature and the concentration of ^{22}Na. Then to analyse this relation we used the function called: *Best Subsets Regression*, from Minitab. This statistical analysis enable to show us which the best predictors for the concentration of ^{22}Na in the atmospheric air are. In order to check out all the possible variables, we are going to use many predictors to check-up which the best adjustment is in order to predict the concentration of ^{22}Na in the atmospheric air.

Vars	R-Sq	R-Sq (adj)	R-Sq (pred)	Mallows Cp	S	Year	Month	Tmm (°C)	Mmm (Month)	Day	Rain (mm/s)	Wind Speed (m/s)
1	35.2	34.1	31.8	28.7	0.18177		X					
1	7.2	5.7	0.8	67.1	0.21753			X				
2	53.7	52.1	49.4	5.5	0.15497			X	X			
2	38.5	36.4	33.0	26.3	0.17857	X			X			
3	58.0	55.9	52.3	1.5	0.14878	X		X	X			
3	54.6	52.3	47.9	6.2	0.15466			X	X		X	
4	58.3	55.5	50.7	3.1	0.14946	X		X	X	X		
4	58.3	55.4	50.4	3.2	0.14955	X		X	X		X	
5	58.3	54.7	48.9	5.0	0.15068	X		X	X	X	X	
5	58.3	54.7	49.2	5.1	0.15071	X		X	X	X		X
6	58.4	54.0	47.4	7.0	0.15195	X		X	X	X	X	X

Graphic 9. Best Subsets Regression (Minitab).

The analysis of the best subsets regression is showed in graphic 9, here we use the monthly mean information from temperature, mm of water rain, the number of raining days and wind speed as well we can see is also the number of the year for check-up if it has an influence in order to predict the concentration of ^{22}Na, all data correspond to 2008 until 2014.

Then the conclusions that we can extract from this analysis is that the best prediction is with 3 variables which also includes the temperature, the number of month, and year, because they have the best R-Sq(adj) and the smallest Mallows Cp. But in this case we also have a great relation with only two variables which predicts practically equal the concentration of ^{22}Na in the atmospheric air but with less variables (is important to predict as much as you can with the minimum number of variables). So we will take this one which predicts better with a minimum number of variables just with the months and the temperature. Then we are going to analyse how it behaves using a graphic with the month, the temperature and the concentration of ^{22}Na.



Graphic 10. Concentration of ^{22}Na in function of temperature each month.

Here we can observe that the months with the warmest temperature are not also the months with the biggest concentration of ^{22}Na, because the main concentration of ^{22}Na it is at 18 km of height (in the tropopause) then what is needed to increase the mass exchange is a differential of temperatures that will create a mass exchange and vertical air flows. In this region of the world, this phenomena happens at the end of spring where the temperature is changing and it is when the biggest exchange between layers takes place. In summer and winter the layers have a stratification phenomenon that is the main reason for the stop of increasing the ^{22}Na concentrations at ground level.

Then we can observe that the temperature as a variable does not have a major effect, but when it is combined with a strong vertical turbulence then is patent that it increases the concentration of ^{22}Na at the ground level, as it can be observed at the month of March were it had a minimum increase of temperature but has the biggest increase of ^{22}Na concentration.

A partial conclusion is that the temperature is related with the concentration of ^{22}Na somehow the temperature is able to affect to the vertical diffusion coefficient of ^{22}Na, as well-known it has many other parameters related with pressures, wind speed, initial concentration of ^{22}Na and others.

5.7. Reanalyse the filters with a 60% of Currie confidence level

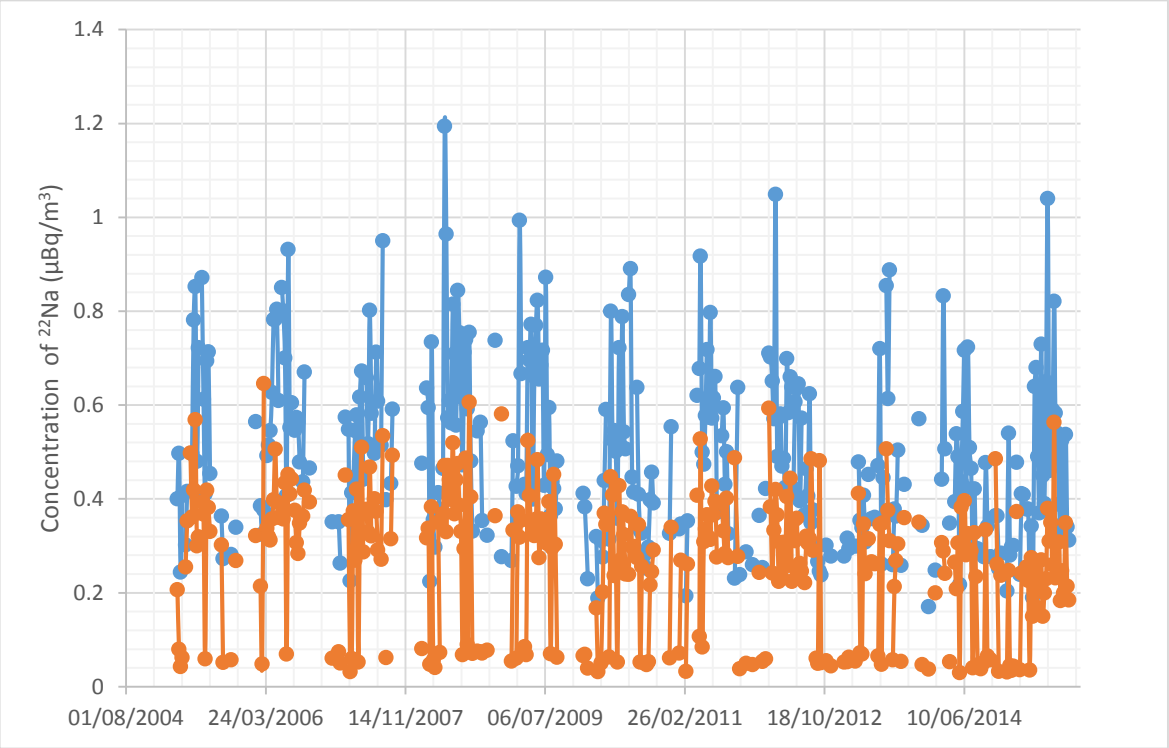
As it has been pointed in section 5.1, the confidence level that has been applied to determine the MDA corresponded to a 95% confidence level. According to this, when all the spectrum were analysed then it was possible to see four situations:

- Activity >> MDA.
- Activity > MDA or similar to MDA.
- Activity < MDA.
- No counts.

In particular, most filters showed an activity greater than the MDA even with 95% confidence level, but up to 25% showed activities close or below MDA. It was decided to accept a lower confidence level, of 60% in order to assess ^{22}Na concentrations even when actually was really low. Here we are going to expose the algorithm that has been created to accomplish this goal. The algorithm had to discriminate between which had more than 60% of probability to exist or not, accepting that the peaks are normally distributed then just we had to compare the confidence interval that have 95% of the probability. The mean point and the MDA. With this we checked if the probability of the MDA was at the point under the 60% of the probability or not, the algorithm returned true or false. In the case that was true then means that the filter worth to be reanalysed. From 573 filters, 142 had to be reanalysed with the 60% of Currie confidence level, approximately 25% of the filters.

This filters were analysed with 60% of Currie confidence level, then another algorithm was created which discriminate the results with an uncertainty higher than 90% and those for the new confidence interval reach the new MDA of 60% of Currie confidence level. The 142 filters reanalysed, 33 of them, were out of range then we consider, that there was not ^{22}Na in the filters.

Then with all this information including all the available data points we made the graphic 11 that shows clearly that the minimum detectable activity of all the filters is near to 0,2 µBq/m^3.



Graphic 11. Concentration of ^{22}Na in front of the time including this with 60% of Curi confidence in blue line, with orange line is the MDA.

In the graphic 11 it is easily possible to diferenciate the data points with a MDA of 95% or 60% of Currie confidence level.

In order to know how behaves the MDA we are going to need an exhaustive study with all the possible variables that affects it to the equations and see how it is that it changes for all the filters and how it does. This will provide us the necessary information about it and what is possible to modify in order to pull down the MDA until the minimum possible.

6. New method for measuring the concentrations of ^{22}Na in LARA

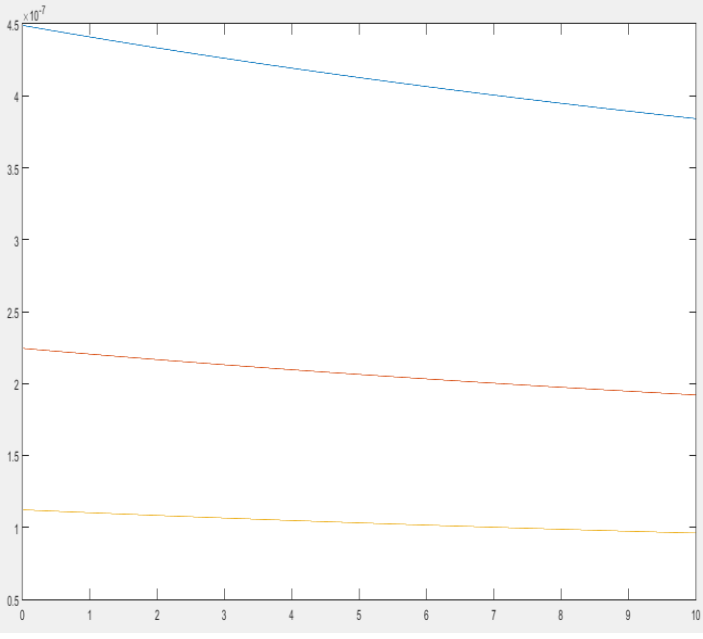
As it has been pointed out in the previous section, many times it is not possible to detect ^{22}Na due to the limitations of the currently used instrumentation and methodology.

To set up a new method to measure ^{22}Na with lower MDA many different approaches can be proposed:

- Increase the counting time to reduce the MDA value.
- Increase the sampling period.
- Increase the amount of the collected aerosols by using an aerosol sampler able to work at higher flow-rates.
- Combine different possibilities.

Since is not possible change the aerosol sampler or increase the sampling period (to avoid the filters saturation) it was decided to explore how to reduce the MDA by increasing the counting time and making a two-weeks sample composed of two filters packed together.

6.1. Analysis of MDA



Graphic 12. At the Y axis is the units Bq/m^3 for the MDA and at the X axis is the numbers of days counting into the gamma detector

The MDA (minimum detectable activity) can be expressed with the equation number (7) then it was recreated with Matlab in order to know the evolution of the typical samples MDA in function of the days that have been into the gamma detector for seeing how it does affect to the MDA. An average filter: with a waiting time of a months, a collection time of a week, a volume of 100000 m^3, 200 counts of ^{22}Na, an efficiency of 0,012, a yield of 99,94%, a count time for the blank of 177800 seconds and a k coefficient at 95% of Currie

confidence level. Then we obtain the blue line for such MDA in function of the counting days.

From the blue line original sampled volume we can observe that the MDA only decrease from 0,45 µBq/m^3 to 0,45 µBq/m^3 in 10 days what is not too much as for all the time and money required for all this days measuring. Then we check up the idea to double the sampled volume and quadruplicate it also, then we obtain respectively the red and yellow lines that decrease about 0,23 and 0,33 µBq/m^3 respectively. These numbers have been calculated from the graphic 12.

Form this numeric analysis we can see that the biggest decrease of the MDA is from 100000 to 200000 m^3 of air sample and will not require too much time in the detector in order to have a detection of the radionuclide. Then it means that we will need to increase the volume of the air sample.

6.2. Optimization of a two-week sample geometry of measurement

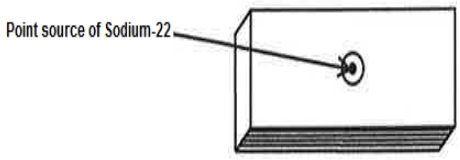


Figure 17. Schematic of the detector and the container with ^{22}Na source at the top

A two-week sample can be made just stacking the two filters inside their own packaging boxes on the germanium detector, however it was foreseen that better results could be obtained by compressing the filter to reduce their volume. In order to check this assumption several experimental measurements were carried out with a ^{22}Na point source (figure 17).

Form the part 4.10.1, we have seen how it had been prepared a standard in order to calibrate de Ge detector. Then from the regression equation for high energies, at the energy of 1274,5 keV (for ^{22}Na) we obtained an efficiency of 1,19 %.

First of all, when we want to compress with 40 tons of pressure (experimental pressure applied to filters) the filter, it must be dried up again to expulse all the humidity that could take during it exposition. If previous step is not realized then the filter could finish in bad conditions.

For checking-up the method to compress filters then available filters from 2014 were used, a sample of 2 filters in the same box at the same time was made and it was measured in different

ways.

The counting time in all the experiments was exactly equal to 10800 seconds (3 hours) in order to minimize the uncertainty of the efficiency. The source of ^{22}Na had in 1st of February of 1993 an activity of 38100 Bq of ^{22}Na. All the uncertainty results given are expressed as:

$$Uncertainty = \pm 2\sqrt{(U'_C)^2 + (U'_A)^2} \qquad \text{(Eq. 14)}$$

Where:

U'$_C$: Is the uncertainty of the counts.

U'$_A$: Is the uncertainty of the source.

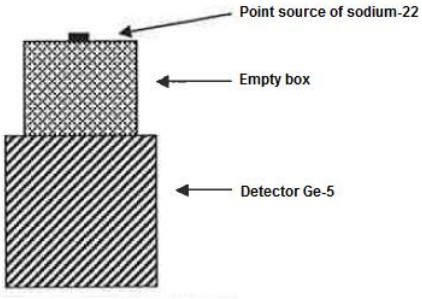


Figure 18. Schematic of the experiment 1

Experiment 1:

In this experiment was used an empty box and the point source of ^{22}Na was placed over in exactly the middle of the box and the measurement was repeated 3 times. It gives an average efficiency of 1,09±0,049 %.

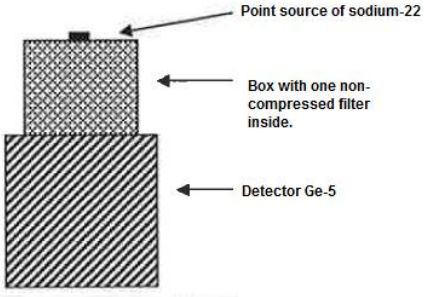


Figure 19. Schematic of the experiment 2

Experiment 2:

In this experiment one used filter with dust (non-compressed), was placed inside the box, over it was located again the source of ^{22}Na exactly like in the experiment 1, the experiment also was repeated 3 times. This second experiment gives an average efficiency of 0,972±0,048 %.

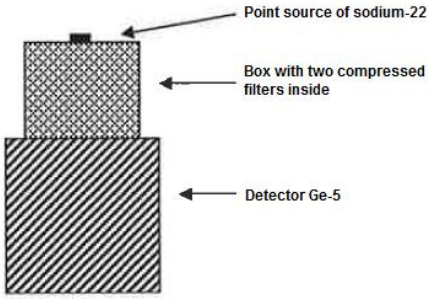


Figure 20. Schematic of the experiment 3

Experiment 3:

In this experiment, the source of ^{22}Na was placed over the box with two compressed filters inside, then was repeated 3 times the experience. This third experiment gave an average efficiency of 1,00±0,045 %.

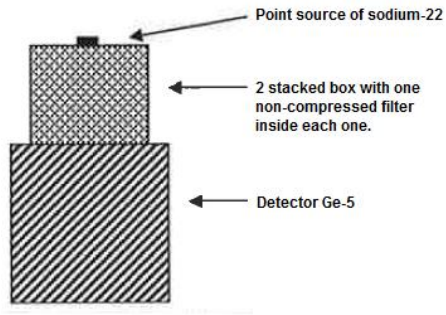


Figure 21. Schematic of the experiment 4

Experiment 4:

In this experiment 2 boxes containing non-compressed filters where stacked with the source at the top. This fourth experiment gave an average efficiency of 0,927±0,042 %.

Description	Efficiency (%)	Uncertainty (%)
Experiment 1	1,09	4,87E-02
	1,08	4,84E-02
	1,09	4,88E-02
Mean experiment 1	**1,09**	**4,86E-02**
Experiment 2	0,969	4,38E-02
	0,978	4,42E-02
	0,969	4,38E-02
Mean experiment 2	**0,972**	**4,39E-02**
Experiment 3	0,994	4,48E-02
	1,01	4,53E-02
	0,999	4,50E-02
Mean experiment 3	**1,00**	**4,50E-02**
Experiment 4	0,9,26E-03	4,21E-02
	0,9,22E-03	4,19E-02
	0,9,31E-03	4,23E-02
Mean experiment 4	**0,9,27E-03**	**4,21E-02**

Table 2. Information about the experiments

The experiment 1 indicates that the efficiency is lower than the calculated for the standard in 8,4% (from 1,19 % to 1,09 %) that have many reasons to be: the standard is with a volumetric distribution while in the experiment a point of source is used. Another is that the distance between the source and the crystal of germanium has been increased, among another parameters being this two the most important. For all this in a future research will be necessary to check up the effect of this two parameters and quantify their effects. It is needed a standard solution of ^{22}Na, and then it will be possible to quantify exactly the efficiency.

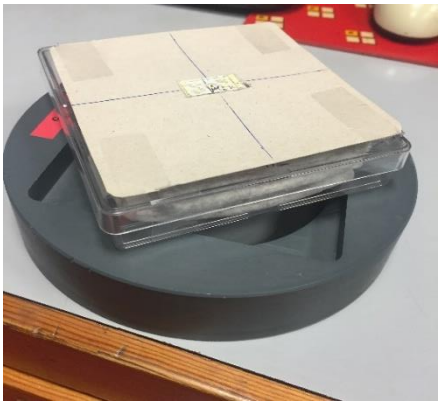


Figure 22. Box with ^{22}Na source and 2 compressed filters inside. Is the configuration for the experiment 3.

Another conclusion of all this experiments is that is more efficient to use 2 compressed filters (experiment 3) than 1 non-compressed filter (experiment 2) or 2 non-compressed filters in two different boxes stacked (experiment 4). In figure 22 is possible to observe a rectangular sheet of paper and over it there is the ^{22}Na source

From all the information and experiments carried out then we have realized about many ways to renew the method for quantify the concentrations of ^{22}Na.
The main improvement is compressing the filters with a pressure about 40 tons in order to be able to place 2 filters inside a single box to reduce the volume of the final sample.

Other improvements that make easier to quantify the quantity of ^{22}Na are:

- To increase the counting time up to 5 days instead of 3, because it decreases the MDA and the uncertainty of the results as it is showed in the graphic 12.
- To use compressed filters instead of non-compressed ones, because the decrease of its efficiency respect to the standard geometry without any filter is of only 8,2 % and 10,7 % respectively to experiments 2 and 3 as is shown at the table 2.

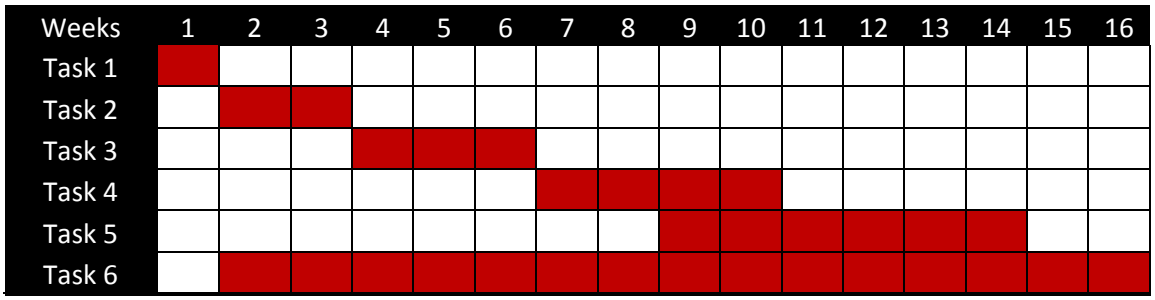
Then the next steps could be:

- Calibrate with a standard of the same geometry than the samples with a certified solution of ^{22}Na, and then calculate the exact efficiency and verify the effect of the sum peak effect.
- Study exhaustively the possibility to perform radiochemical separation of ^{22}Na and measure it by beta counting.

This method is considered still unfinished because it has not been possible to validate it with real samples, but the project covered the main steps to tune up a measurement method for ^{22}Na in the atmospheric air.

7. Budget

7.1. The costs in time of work



Gantt Diagram. This diagram starts at the week 37 of the year 2015 and finish at the 2nd week of the year 2016.

- Task 1: Find articles and another information sources and synthetize their ideas.
- Task 2: Collect information of previous filters.
- Task 3: Analyse the information from filters and relate it with other variables.
- Task 4: Propose a new method to analyse and apply it.
- Task 5: Calibrate the peak of ^{22}Na and validate the information.
- Task 6: Redaction of the report.

Remarkable information: The task 6 was made ever in spare time when was possible in order to make the redaction while I was working and be more efficient.

There was an average of 5 hours every day of work with 5 days every week during 16 weeks the cost in time is of 400 hours in the facilities for making tasks 1 to 5. Additionally we have to add a 250 hours for the task 6, this makes a total of 650 hours. Here is not quantified time to read previous information, the time to take first meeting with the facilities and another meetings with tutor and the personal that supported this work.

The personal of INTE have an average support of 1 hour day that multiplied for 16 weeks, 5 days per week are 80 hours of work.

7.2. How I have done the work

Task 1

The task 1 started in summer but it was an irregular time and it was not completed until the first week.

Task 2

The filters between years 2001 and 2015 have been analysed to know atmospheric radiation at the marked point by *INTE* facilities, to prevent the consequences from a dramatic increment of radiation levels in the city. Then the workers from *INTE* saved the spectrum in a data base that contains all the information for ^{22}Na and another radionuclides, in total are almost 800 filters. Had to be reanalysed all the filters from this place with the program Genie2000, return the information in PDF file about many radionuclides and also had to be rewritten all the information about ^{22}Na in Excel to be able to make the pertinent statistical analysis. The total time spent for doing that was about two whole weeks all the process to each one cost about 5 minutes. However, with all this information we started the process for tuning up a measurement method for ^{22}Na in the atmospheric air.

Task 3

With all the information from the reports in Excel pages then we started to recompile information from many sources about the sunspots, the mm of rain, the wind speed, the concentration of ^{7}Be for all the time that we were studying or what was available in the way that also was available (normally monthly averages). Then we correlated with the program Minitab that is a statistical program basic and simple one but enough in order to see correlations, boxplots and regressions. Also was necessary to evaluate the evolution of the MDA in function of time and volume and it was simulated with the program Matlab with a really good accuracy level, in this case for 10 days of counting time it make the simulation with a million divisions making possible to not see lineal parts in the simulation.

Task 4

The proposed method was not possible to check out without the next task that is to calibrate the efficiency of the detector and if it is not well then have to be proposed a new method and the iterate until getting the new method that match well the efficiency.

Task 5

This process required to try the new geometry and check its efficiency and how it changes and trying a few samples, it takes a few hours in order to detect in all the possible configurations.

Task 6

This report was started the second week in order to do not miss any information or detail. All what was finished such as graphic, conclusions, information that was searched, the shortcuts

and another, was written a soon as was possible to start into this report. Ending at 14 of January of 2016.

7.3. Costs

Here we are going to break down the different kinds of cost for all what was used in this project, form hours of the working power and the needed materials.

7.3.1. The cost of the working time

The standard price for a junior engineer is stablished as 12 € per hour and is with what will be counted, then the standard price for a working hour of a senior engineer is 30 €. Whit all this information we can know how much does it cost.

All this will be represented in the following table:

Operator	Time (hours)	Price (€/hour)	Total amount (€)
Student	650	12	7800
INTE personal	80	30	2400
		Total cost:	**10.200 €**

7.3.2. The cost of used material

In this project it was necessary to use 13 times the gamma detector in order to measure the radioactive source of ^{22}Na in many geometries 9 times and 4 times the compressed filters. All this had a cost of two weeks using the detector 5 with it associate cost of using 2,5 L of liquid nitrogen for refrigerate the coldfinger and the cost of the detector in order to proceed to its amortization. Also we needed 4 high volume filters, 2 of them compressed (with the same price) in order to procced to analyse them with the radioactive source.

The unique utility that has been used of electricity with an average price of 0,13 €/kwh - we used the detector 336 hours (2 weeks) with an electric power consumption of 1000 W then the total cost of the electricity was of 43,36€

Material	Quantity	Price (€/units)	Total amount
N_2 used (L)	35	13,5	472,5 €
Gamma detector (used times)	13	37,5	487,5 €
High volume filters	4	13	52 €
Total cost:			1012 €

7.4. Total cost of this project

Here is the sum of all the cost and need of this project in order to give just one number that counts everything that has been used while this project was running.

Cost of time	10.200 €
Cost of materials	1012 €
Cost of electricity	43,36 €
Total cost	**11.255,36 €**

It is easy to check that most part of the cost of this project was cost of time, exactly from the student that is almost 70% of the total cost of project and the conjunction of all the working power have the cost of 90% off all the project.

8. Environment

We consider the waste that has been generated is minimum because what was used for this experiment are not dangerous for the environment and they are going to be stored for many years, finally they will be given to the EcoCat that is a enterprise which works with the laboratory and weekly takes the waste from the laboratories.

The filters cannot be considered a radiological waste due its activity is really low because its origin and they are not contaminated.

The electricity that was used is recommended by the Catalan office of climatic change that it has to be counted how much CO_2 has been generated in this project with an exchange factor between them of 248 g CO_2/kWh.**[23]**

We consumed 336 kWh in the detector and then with the previous ratio exchange we have that have been generated 83 kg of CO_2 and it is the unique ecological impact of this project.

Conclusions

This is the first study about ^{22}Na in Spain and this data shows important information about the behaviour and variables of influence on this radionuclide.

According to the aims of this works it has been studied the temporal evolution of ^{22}Na, which is clearly cyclic along the year due to the differential of temperatures between the troposphere and the stratosphere during a whole year. The concentration of ^{22}Na increases when the hot air from the lower layer mixes with the upper air nearer to the tropopause where the ^{22}Na is produced, and this exchanging air pull down the radionuclide (with the falling mass of air) doing possible to detect it at the ground level. Another variable of influence is the precipitation, when it rains ^{22}Na is washed up. The solar cycle affect the concentration of ^{22}Na to a lesser extent. The wind speed at the ground level does not have any effect on the concentration of ^{22}Na.

During the winter ^{22}Na concentration is usually very low and in most cases it is no possible to assess it by means of the currently used instrumentation and methodology at LARA. To optimize the ^{22}Na determination and according to the aims of this project, a new methodology has been proposed. Since it is not possible to increase the sampling period nor to increase the flow-rate of the aerosol sampler, to achieve a lower MDA the new methodology is based on two-week samples made of two compressed weekly filters (instead of single weekly samples) measured during a longer counting time in the available detectors. The best measurement configuration has been selected using a ^{22}Na point source to assess the effect on the detection efficiency of the different attenuations and distance to detectors of the studied configurations. It has been also checked that the currently used calibration curve is valid for the proposed new counting geometry.

The new methodology is an easy and non-expensive solution that allows achieving a lower MDA that can be applied even to cold seasons in order to detect and quantify the ^{22}Na even when the concentration of this radionuclide is really low.

Acknowledgment

Thanks to *Maria Amor Duch,* for her support and so much help with needed books and the correction and the order of this project, to orientate correctly the work and many tips that helped for the realization of this project.

Thanks to *Isabel Serrano,* for finding all the old data about the filters, to facilitate many information about where to find the correct information related with the project and for preparing all what was necessary in order to collect the needed big amount of reports from all the filters.

Thanks to *Małgorzata Winiarska*, for all the support that gave during preparation of this project and for the help in the correction of this one.

Bibliography

[1] By N. BHANDARI, D. LAL and RAMA. **Stratospheric circulation studies based on natural and artificial radioactive tracer elements.** Tata Institute of Fundamental Research, Colaba, Bombay-5. Manuscript received on 11 November of 1965

[2] Sylwia Błazej • Jerzy W. Mietelski. **Cosmogenic ^{22}Na, ^{7}Be and terrestrial ^{137}Cs, ^{40}K radionuclides in ground level air samples collected weekly in Kraków (Poland) over years 2003–2006**. J Radioanal Nucl Chem (2014) 300:747–756 DOI 10.1007/s10967-014-3049-6

[3] Magdalena Długosz-Lisiecka • Henryk Bem. **Determination of the mean aerosol residence times in the atmosphere and additional ^{210}Po input on the base of simultaneous determination of ^{7}Be, ^{22}Na, ^{210}Pb, ^{210}Bi and ^{210}Po in urban air**. J Radioanal Nucl Chem (2012) 293:135–140 OI 10.1007/s10967-012-1690-5

[4] H. Tokuyama & S. Igarashi. **Seasonal Variation in the Environmental background Level of Cosmic-Ray-Produced 22Na at Fukui City, Japan.** J. Environ. Rndioactivity**,** Vol. 38, No. 2, pp. 147-161, 1998

[5] SYLWIA GRABOWSKA, JERZY W. MIETELSKI, KRZYSZTOF KOZAK and PAWEŁ GACA. **Gamma Emitters on Micro-Becquerel Activity Level in Air at Kraków (Poland).** *Journal of Atmospheric Chemistry* **46:** 103–116, 2003.

[6] Rimvydas Jasiulionis, Herbert Wershofen. **A study of the vertical diffusion of the cosmogenic radionuclides, 7Be and 22Na in the Atmosphere.** Journal of Environmental Radioactivity 79 (2005) 157–169.

[7] A.-P. Leppänen, I.G. Usoskin, G.A. Kovaltsov, J. Paatero. **Cosmogenic ^{7}Be and ^{22}Na in Finland: Production, observed periodicities and the connection to climatic phenomena.** Journal of Atmospheric and Solar-Terrestrial Physics (2012).

[8] Philipp Steinmann*, Michael Zeller, Pierre Beuret, Giovanni Ferreri, Sybille Estier. **Cosmogenic ^{7}Be and ^{22}Na in ground level air in Switzerland (1994-2011**). Journal of Environmental Radioactivity 124 (2013) 68e73

[9] Weihua Zhang • Jing Yi • Pawel Mekarski ·Ian Hoffman • Kurt Ungar • Ari-Pekka Leppänen**. A system for low-level the cosmogenic ^{22}Na radionuclide measurement by gamma–gamma coincidence method using BGO detectors.** J Radioanal Nucl Chem (2011) 287:551–555 DOI 10.1007/s10967-010-0758-3

[10] University of Copenhagen, Niels Bohr institute. **Definition of cosmogenic isotopes.** http://www.iceandclimate.nbi.ku.dk/research/past_atmos/cosmogenic_isotopes/ consulted on 17 of September of 2015.

[11] M-M Bé, V. Chisté, C. Dulieu, X. Mougeot**.Table of radionuclides (Vol. 5-A=22 to 244).**

ISBN-13 978-92-822-2234-8 (Vol.5) Page 1

[12] M-M Bé, V. Chisté, C. Dulieu, X. Mougeot**.Table of radionuclides (Vol. 5-A=22 to 244).** ISBN-13 978-92-822-2234-8 (Vol.5) Page 6

[13] Xavier Ortega Aramburu y Jaume Jorba Bisbal. **Radiaciones ionizantes, utilización y riesgos (Vol.1)**. ISBN 84-8301-170-0 has been used topics 1, 2, 3 and 4.

[14] Xavier Ortega Aramburu y Jaume Jorba Bisbal. **Radiaciones ionizantes, utilización y riesgos (Vol.2)**. ISBN 84-8301-168-9 has been used topic 5.

[15] Klaus Froehlich. **Environmental radionuclides tracer and timers of terrestrial process.** Elsevier ISBN 978-0-08-043873-3. Pg 9 and 10.

[16] C. Papastefanou. **Radioactive aerosols.** Elsevier ISBN 978-08-044075-0 Pg 3.

[17] J. Caparthy. **Muons New Research.** Nova Sciences Publishers, Inc. ISBN 1-59454-175-2. Pages from preface.

[18] British encyclopaedia. Sodium (Na) http://www.britannica.com/science/sodium consulted on 22 of October of 2015

[19] NASA, Sunspots. http://image.gsfc.nasa.gov/poetry/workbook/sunspot.html consulted on 30 of September of 2015

[20] Canberra. **Extended Range Coaxial Ge Detectors (XtRa).** Available at http://www.canberra.com/products/detectors/pdf/XtRa-detectors-C40024.pdf, it is a page from the producer of gamma detectors for LARA facilities. Consulted at the day 05/10/2015.

[21] Articles 35 and 36 of the EUROATOM and the details of the articles, http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32000H0473&from=EN Consulted at the day 21/10/2015.

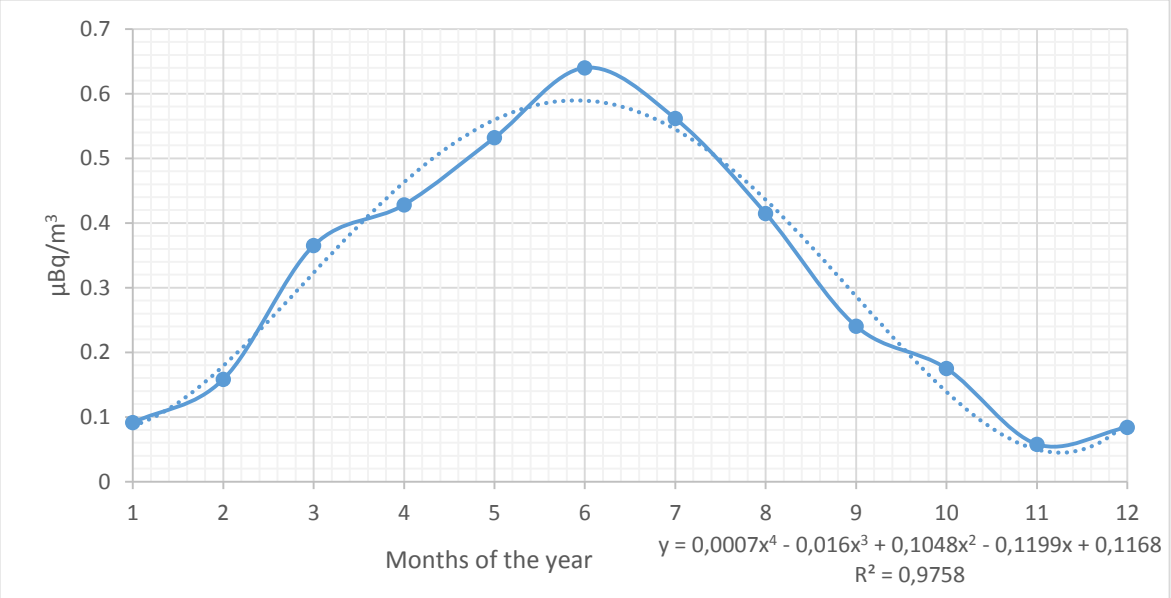
[22] Camberra. **Genie2000 customization tools manual**. Genie algorithms, topic 3. This manual does not have any identification code, for take the information if this one you need to go to www.camberra.com and then is possible to order one.

[23] Catalan office of climatic change, **Practical guide for the calculus of emissions of gases with hibernacula effect** *(GEH)*, Version of March of 2014 page 10.

Annexes

Annex A

Graphic from the equation 13



Graphic from the equation 13. Concentration of ^{22}Na versus months of the year. Where the continuous line with 12 dots is the concentration as was observed in the boxplot number 3 and the pointed line is the regression of this points.

Annex B

There is two kinds of sum peak, because of random and by coincidence:

The first one is when a beta emission is mixed with two gamma emissions creating a bigger counts that what really is. The way to avoid is with the distance from the detector as much distance less peak you will have. For the case of ^{22}Na yet has to be determine.

The second one is the coincidence of two gamma radiations happening at the same time that leaves the energy at the same time to the detector. The way to avoid this problem is increasing the speed of counting from the detector in order to spare as much is possible the gamma radiations in time decreasing the probability that two of them will impact at the same counting time.