



*Department of Nuclear Physics*  
AMS and Radiation Physics Group  
University of Lund

**DEVELOPMENT OF A METHOD TO MEASURE  
THE CONCENTRATION OF  $^{14}\text{C}$  IN THE STACK  
AIR OF NUCLEAR POWER PLANTS BY  
ACCELERATOR MASS SPECTROMETRY (AMS)**

Kristina Stenström • Bengt Erlandsson • Ragnar Hellborg •  
Kjell Håkansson • Göran Skog • Anders Wiebert

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Department of Nuclear Physics  
Sölvegatan 14  
S-223 62 Lund  
Sweden

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K Stenström  
B Erlandsson  
R Hellborg  
K Håkansson  
G Skog  
A Wiebert

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Development of a method to measure the concentration of C-14 in the stack air of nuclear power plants by accelerator mass spectrometry (AMS)

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**Abstract:** C-14, a pure low-energetic beta-emitter, is produced through various nuclear reactions in nuclear power plants. Some of this C-14 is air-borne and is transported via the ventilation system through the stack of the power station and is integrated in living matter in the surroundings of the plant. The long half-life of the isotope ( $T_{1/2}=5730$  years) and the biological importance of carbon may lead to a not negligible contribution to the radiation dose for those living in the neighbourhood of nuclear power plants. C-14 has earlier been measured radiometrically with mainly two different methods, using proportional counters or liquid scintillators. In this report a new method is described, using an accelerator based technique, accelerator mass spectrometry (AMS). This technique has at least three advantages over the radiometrical methods. It requires only a few litres of gas per sample, which is 100-1000 times less compared to the radiometrical methods. It is insensitive to the beta and gamma rays from other radioactive isotopes in the stack air. The measuring time with AMS, about 20 minutes per sample, is considerably shorter compared to the radiometrical methods, which demand several hours per sample. The integrity of the AMS method is high and it might be convenient for regulatory supervision.

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Karin Stenström, Bengt Erlandsson, Ragnar Hellborg, Kjell Håkansson,  
Anders Wiebert  
Department of Nuclear Physics, University of Lund, Sölvegatan 14, S-223 62 Lund,  
Sweden

Löran Skog  
Department of Quaternary Geology, University of Lund, Tornavägen 13,  
S-223 62 Lund, Sweden

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Abstract.....	1
1. Introduction.....	1
2. Earlier radiometrical methods.....	3
2.1 Sampling methods.....	3
2.2 Methods to determine the activity concentration .....	4
2.3 Examples .....	6
3. The AMS method.....	7
3.1 A general description.....	7
3.2 The stack air sampler.....	8
3.2.1 Construction.....	8
3.2.2 Function.....	10
3.3 Sample preparation .....	11
3.3.1 The carbonatization system.....	11
3.3.1.1 Construction.....	11
3.3.1.2 Function.....	13
3.3.2 The graphitization system.....	13
3.3.2.1 Construction.....	14
3.3.2.2 Function.....	16
3.4 The AMS facility.....	18
3.4.1 Construction.....	18
3.4.2 Function.....	20
4. Calculations.....	22
5. Results.....	23
6. Error estimates .....	26
7. Conclusions .....	28
8. References.....	29

## Abstract

$^{14}\text{C}$ , a pure low-energetic beta-emitter, is produced through various nuclear reactions in nuclear power plants. Some of this  $^{14}\text{C}$  is air-borne and is transported via the ventilation system through the stack of the power station and is integrated in living matter in the surroundings of the plant. The long half-life of the isotope ( $T_{1/2}=5730$  years) and the biological importance of carbon may lead to a not negligible contribution to the radiation dose for those living in the neighbourhood of nuclear power plants.  $^{14}\text{C}$  has earlier been measured radiometrically with mainly two different methods, using proportional counters or liquid scintillators. In this report a new method is described, using an accelerator based technique, accelerator mass spectrometry (AMS). This technique has at least three advantages over the radiometrical methods. It requires only a few litres of gas per sample, which is 100-1000 times less compared to the radiometrical methods. It is insensitive to the beta and gamma rays from other radioactive isotopes in the stack air. The measuring time with AMS, about 20 minutes per sample, is considerably shorter compared to the radiometrical methods, which demand several hours per sample. The integrity of the AMS method is high and it might be convenient for regulatory supervision.

## 1. Introduction

$^{14}\text{C}$  is a radioactive isotope (half-life 5730 years) produced naturally in the atmosphere by secondary neutrons in the cosmic radiation, but also in nuclear power plants. In the atmosphere the main part of the carbon is in the form of carbon dioxide (330 ppm), chiefly with the stable isotopes  $^{12}\text{C}$  (98.89 %) and  $^{13}\text{C}$  (1.11 %). The  $^{14}\text{C}$  isotope constitutes only about  $10^{-10}$  % of the total amount of carbon. Around nuclear power plants the  $^{14}\text{C}$  concentration can be higher, which has been reported earlier by for instance Levin et al [1], Loosli and Oeschger [2], McCartney et al [3] and Obelic et al [4].

$^{14}\text{C}$  is produced in a reactor by neutron induced reactions in the fuel, the coolant and structural materials, mainly with the reactions  $^{17}\text{O}(n,\alpha)^{14}\text{C}$  and  $^{14}\text{N}(n,p)^{14}\text{C}$ .  $^{17}\text{O}$  exists naturally in the fuel and in the coolant, while  $^{14}\text{N}$  may for example occur as an impurity in the fuel and as a gas. In Pressurised Water Reactors (PWR), like the Ringhals reactors no. 2, 3 and 4, hydrogen is added to the coolant and therefore the produced radioactive carbon isotope is expected mainly to form hydrocarbons. In the Forsmark plant, with three Boiling Water Reactors (BWR),  $^{14}\text{C}$  tends to form carbon dioxide by reactions with radiolytically produced oxygen.

The amount of  $^{14}\text{C}$  produced and released from a power plant can roughly be estimated, but because of the biological importance of carbon and the long half-life of  $^{14}\text{C}$  it is important and interesting not only to calculate but also to measure the releases. There has been only a few reports on the measurement of  $^{14}\text{C}$ -releases from nuclear power plants. One reason is the difficulty to measure the activity concentration of  $^{14}\text{C}$  in the ventilation air by radiometrical methods, since  $^{14}\text{C}$  is a pure  $\beta$ -emitter with a low maximal energy (156 keV). Another reason is the high concentration of other  $\beta$ -emitters like fission and activation products in the ventilation air.

The aim of this investigation is to develop a method to measure the concentration of  $^{14}\text{C}$  in the stack air by accelerator mass spectrometry (AMS). We have constructed and built a continuously operating stack air sampler. To extract carbon dioxide and hydrocarbons from the sampled air, these gases are caught in carbonate form in an off-line system. The carbonate sample is then transformed to elementary carbon in a graphitization system. The relative occurrence of  $^{14}\text{C}$  in carbon is determined at the AMS facility at the Department of Physics in Lund. A typical measuring time at the accelerator is 20 minutes per sample. Several samples of stack air have been collected from both a PWR (in Ringhals) and a BWR (in Forsmark). The  $^{14}\text{C}$  concentration in these samples has been measured with the new method.

In the following sections some of the earlier methods used to determine the activity concentration in the stack air of nuclear power plants will be given account of, followed by a more detailed description of the new detection technique of  $^{14}\text{C}$  from nuclear power plants by the AMS facility in Lund.

For further information about the results see "Measurement of the  $^{14}\text{C}$  concentration in the stack air of two Swedish nuclear power plants by accelerator mass spectrometry. A one year study of a PWR in Ringhals and a BWR in Forsmark" by Stenström et al [5].

## 2. Earlier radiometrical methods

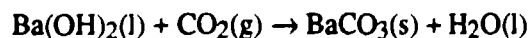
In a report by Snellman [6] different sampling and counting methods of  $^{14}\text{C}$  in discharges from nuclear facilities are accounted for. Sections 2.1 and 2.2 below summarise this report. Section 2.3 exemplifies some specific methods used by Hayes and MacMurdo [7], Hertelendi et al [8], Hesböl and Gebert [9] and Kunz [10].

### 2.1 Sampling methods

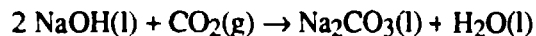
When measuring the activity concentration of  $^{14}\text{C}$  it is necessary to separate the carbon from the rest of the gases in the air sample. In radiometrical activity measurements one must get rid of the radioactive noble gases whose activity usually is much higher than that of  $^{14}\text{C}$ . Furthermore,  $^{14}\text{C}$  is a pure  $\beta$ -emitter with a low maximal energy of the emitted  $\beta$ -particles (156 keV) which requires that the sample must not contain interfering radionuclides. A common way is to collect the carbon by trapping the carbon dioxide. To catch all carbon, the carbon compounds besides the  $\text{CO}_2$ , such as  $\text{CO}$  and  $\text{CH}_4$ , must be converted into  $\text{CO}_2$ . Catalytically, this can be done for instance by drawing the gas through  $\text{CuO}$  at  $400\text{-}800^\circ\text{C}$  or through a mixture of  $\text{PdAl}$  and  $\text{PtAl}$  at  $600\text{-}800^\circ\text{C}$ . The latter is the more effective one.

*Molecular sieving* in crystalline synthetic zeolites, is one way to collect the airborne  $^{14}\text{C}$  releases.  $^{14}\text{CO}_2$  can selectively be collected in molecular sieves but should be preceded by a water vapour trap, such as silica gel, since the zeolite also traps water molecules, resulting in poor  $\text{CO}_2$  absorption efficiency. The  $^{14}\text{CO}_2$  is removed from the sieve, by for example heating the zeolite to  $200\text{-}350^\circ\text{C}$ . By washing with a dry gas such as nitrogen, the  $\text{CO}_2$  is transported away and then led through a  $\text{Ba}(\text{OH})_2$  solution to form carbonate.

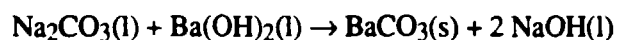
A number of different *chemical absorption methods*, all based on  $\text{CO}_2$  absorption in alkaline solids or solutions, can be used. Starting with the alkaline solutions, there are two distinguishable methods, the direct alkaline process and the double alkaline process, both well known chemical reactions. The direct alkaline process uses dilute solutions such as  $\text{Ca}(\text{OH})_2$  or  $\text{Ba}(\text{OH})_2$ , and the reaction taking place when  $\text{CO}_2$  is bubbled through the solution is, in the case of  $\text{Ba}(\text{OH})_2$ :



Since solid carbonate is precipitated, plugging problems are frequent in the sampling vessels containing the alkali solutions. With the double alkali process this problem is avoided. Having for instance NaOH, the water dissolvable Na<sub>2</sub>CO<sub>3</sub> is formed:



1 or 2 M solutions are most frequently used. For an efficient sampling it is suitable to use two or more fritted gas washing bottles in series so that the contact surface between the gas and the solution is large and that the contact time is long. Carbonate is precipitated by adding for instance Ba(OH)<sub>2</sub>:



Instead of Ba(OH)<sub>2</sub>, BaCl<sub>2</sub> can be added to form BaCO<sub>3</sub> and NaCl.

Solid alkali hydroxides are in many cases preferable to the solutions, since smaller vessels and higher gas streams can be used. It requires less operator attention and is easier to transport. For all solid absorbents water vapour must be removed from the gas before the reaction, since the moisture decreases the absorbent's efficiency. Solid Ca(OH)<sub>2</sub> made through reaction of CaO and H<sub>2</sub>O has been found to have high efficiency at 350-450°C. To release the CO<sub>2</sub> the absorber is heated to 900-950°C. Ascarite, NaOH on a solid support, is another absorbent. When CO<sub>2</sub> is absorbed Na<sub>2</sub>CO<sub>3</sub> is formed. It is important to remove water vapour in the sampled gas before the reaction takes place in order to keep a high efficiency and to prevent the NaOH from being dissolved and the tube from becoming cloggy. The CO<sub>2</sub> can be evolved by adding some acid.

## 2.2 Methods to determine the activity concentration

Before using *gas proportional counting* technique the sample gas, that is CO<sub>2</sub> or CH<sub>4</sub> or a mixture of carbon dioxide and hydrocarbons in a non-active gas, must be purified using cryogenic or gas chromatographic procedures in order to get rid of interfering radio nuclides. Several millilitres to a few litres of gas are used. Gas proportional counting has high counting efficiency and uses pulse height discrimination. Using anti coincidence detectors and multichannel analysers the efficiency can be as high as 95 % with a low background.

*Liquid scintillation counting* also requires purification from interfering radio nuclides. The carbon is precipitated in carbonate form and is after washing, filtering and drying mixed with a scintillation solution. In order to homogenise the solution the mixture is



shaken in an ultrasonic vibrator. Normally up to 2 g of the precipitate can be mixed with 20 ml of scintillation solution.

*Solid source counting*, i.e. using a scintillation detector for solids, is possible to use, but has very low counting efficiency.

Tschurlovits et al [11] have made a comparison of the methods mentioned above for measuring  $^{14}\text{C}$ . Common to all the radiometrical methods is that the measuring time is several hours. The comparison is shown in table 1 below.

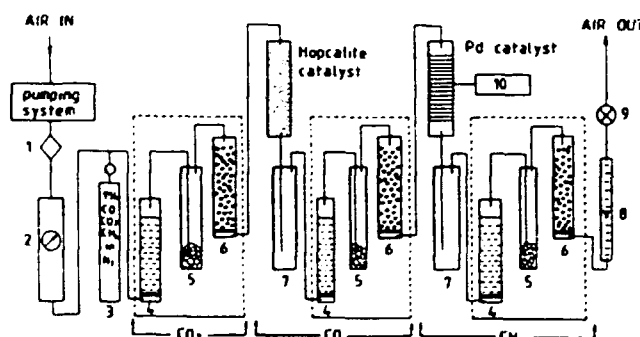
	Internal Gas Proportional Counting	Liquid Scintillation Counting Benzene	Liquid Scintillation Counting $\text{BaCO}_3$	Solid Source Counting $\text{BaCO}_3$
Amount of carbon (g)	1	1	0.5	0.125
Corresponding air volume ( $\text{m}^3$ )	7	7	4	1
Counting efficiency (%)	95	80	35	1.8
Background (counts/min)	23	40	28	7
Lowest detectable concentration (LDC) ( $\text{mBq}/\text{m}^3$ )	5	8	32	1221

*Table 1 Comparison between different radiometrical methods for  $^{14}\text{C}$  measurements [11]*

### 2.3 Examples

Hayes and MacMurdo [7] use a chemical absorption method and liquid scintillation counting. The stack gas is flowing through a LiOH carbon dioxide absorber at about 200 cm<sup>3</sup>/min. Adding HCl the carbon dioxide is released in a closed circulating system, whereupon it is reabsorbed in a NaOH solution. Heating the NaOH solution and adding BaCl<sub>2</sub>, BaCO<sub>3</sub> is precipitated. If there is any gamma activity in the BaCO<sub>3</sub>, the carbon dioxide is released by acid and then reabsorbed and reprecipitated. Dissolving the BaCO<sub>3</sub> with HCl and using a counter current flow of liquid scintillation solution the CO<sub>2</sub> is scrubbed with a spinning band column. Liquid scintillation is then used for counting the <sup>14</sup>C in the sample.

Hertelendi et al [8] have studied the effluents from the Paks nuclear power plant in Hungary using another chemical method for oxidising the different carbon compounds to carbon dioxide and absorbing it. Figure 1, taken from reference [8], features the system.



**Figure 1** Layout of the differential <sup>14</sup>C sampler used by Hertelendi et al [8]

This is a differential <sup>14</sup>C sampler where the amount of <sup>14</sup>C can be studied in CO<sub>2</sub>, CO and hydrocarbons separately. (1) is an aerosol filter, (2) a gas meter, (3) a carrier gas, (4) bubblers containing 400 ml 3 M NaOH solution, (5) drop catchers, (6) drying columns filled with silica gel, (7) buffer flasks to prevent the catalyst from NaOH contamination, (8) a flow meter and (9) a regulating valve. The Hopcalite catalyst at ambient temperature oxidises the CO and the Pd catalyst at 600 °C converts the hydrocarbons into CO<sub>2</sub>. With this construction CO<sub>2</sub> will be absorbed in the first bubbler with NaOH, CO in the second and hydrocarbons in the third. Both low-level gas proportional counting and liquid scintillation counting have been used determining the <sup>14</sup>C activity.

Hesböl and Gebert [9] oxidise the carbon species with a catalyst, catches the carbon dioxide by leading it through a bubbler containing NaOH and precipitates BaCO<sub>3</sub> by addition of 1 M BaCl<sub>2</sub>. The barium carbonate is filtered, weighed, dried at 100 °C for two hours, pulverised in a mortar, weighed and mixed with gel and scintillation liquid, shaken in ultra sound and finally measured by liquid scintillation.

Kunz [10] uses the gas proportional counting method. To prepare the sample the gas is drawn through a catalyst at 600°C consisting of PdAl and PtAl pellets to oxidise all carbon species. Water vapour is then removed by leading the gas through a tube with Drierite whereupon the carbon dioxide is absorbed in 25 g of 8- to 20-mesh Ascarite. The CO<sub>2</sub> is released again from the Ascarite with acid, then helium is bubbled through the mixture carrying the evolved CO<sub>2</sub> to a liquid N<sub>2</sub> trap where it is collected and measured before being placed in the internal gas proportional counter.

### **3. The AMS method**

This section will start with a general description of the Lund system, then in detail give an account for the stack air sampler, the sample preparation system and finally the AMS facility.

#### **3.1 A general description**

The tool for AMS is the Pelletron tandem accelerator at the Department of Physics in Lund. The accelerator is equipped with a caesium sputtering ion source of the ANIS type [12]. This kind of ion source requires that the sample is in a solid compact form in order to produce a quickly stabilising, negative, intensive and long-lived ion beam. Consequently the carbon has to be extracted from the air sample and converted into graphite.

Stack gas is continuously collected during a two week period by a stack air sampler. The sample is stored in a balloon of 50 litres. The balloon is sent to Lund where as a first step a few litres of the gas are mixed with a <sup>14</sup>C-free carrier of carbon dioxide. Adding the <sup>14</sup>C-free carbon dioxide to the sample reduces the counting rate of <sup>14</sup>C in the accelerator's particle detector, and reduces the errors introduced by variations in the carbon dioxide content of the stack air. After the carrier gas has been added all carbon compounds are oxidised to carbon dioxide, whereupon the gas mixture is led through a tube filled with Ascarite (NaOH on a solid support). The carbon dioxide is trapped within the Ascarite since it is converted to solid sodium carbonate, while the other gas compounds are not

affected by the Ascarite and therefore pass right through it. The sodium carbonate is then acidified inside an evacuated glass tube so that the trapped carbon dioxide is evolved. The carbon dioxide is then mixed with hydrogen gas. With the help of a catalyst, in this case iron powder at 650°C, the gas mixture is converted into a few milligrams of graphite while evolving water vapour. The graphite is formed on top of the iron powder. Finally when the reduction is completed, the carbon-iron mixture is pressed into a sample holder suiting the accelerator's ion source.

The ion source forms an ion beam from the carbon atoms on the graphite surface. By applying electric and magnetic fields along the beam line ions with different masses are separated and the relative abundance of the carbon isotopes  $^{13}\text{C}$  and  $^{14}\text{C}$  is determined. Each sample requires about 20 minutes in measuring time.

### **3.2 The stack air sampler**

The demand on the stack air sampler is that it should continuously, during a fortnight, collect stack air and at the same time fill a 50 litre balloon with a fraction of the air. It was required from Vattenfall AB that the collecting of the air samples should be absolutely continuous, hence the rather complicated construction of the stack air sampler.

#### **3.2.1 Construction**

The sampling system consists of a double-acting cylinder (A) (figure 2) with a volume of 5 litres. Each end is via a particle filter (B) connected to the monitoring system of the stack. When the upper volume is filled the lower one is emptied. Via a pressure cylinder (C) and a solenoid valve (D) the air in cylinder (A) is pushed out into the room where the sampler is situated. During an interval of the cycle of emptying, the gas in the pressure cylinder is pushed into a balloon (E). This one contains 50 litres and is filled during a fortnight (or some other adjustable period). The balloons are 5-layer gas sampling bags manufactured by Calibrated Instruments Inc. (200 Saw Mill River Road, Hawthorne, New York 10532).

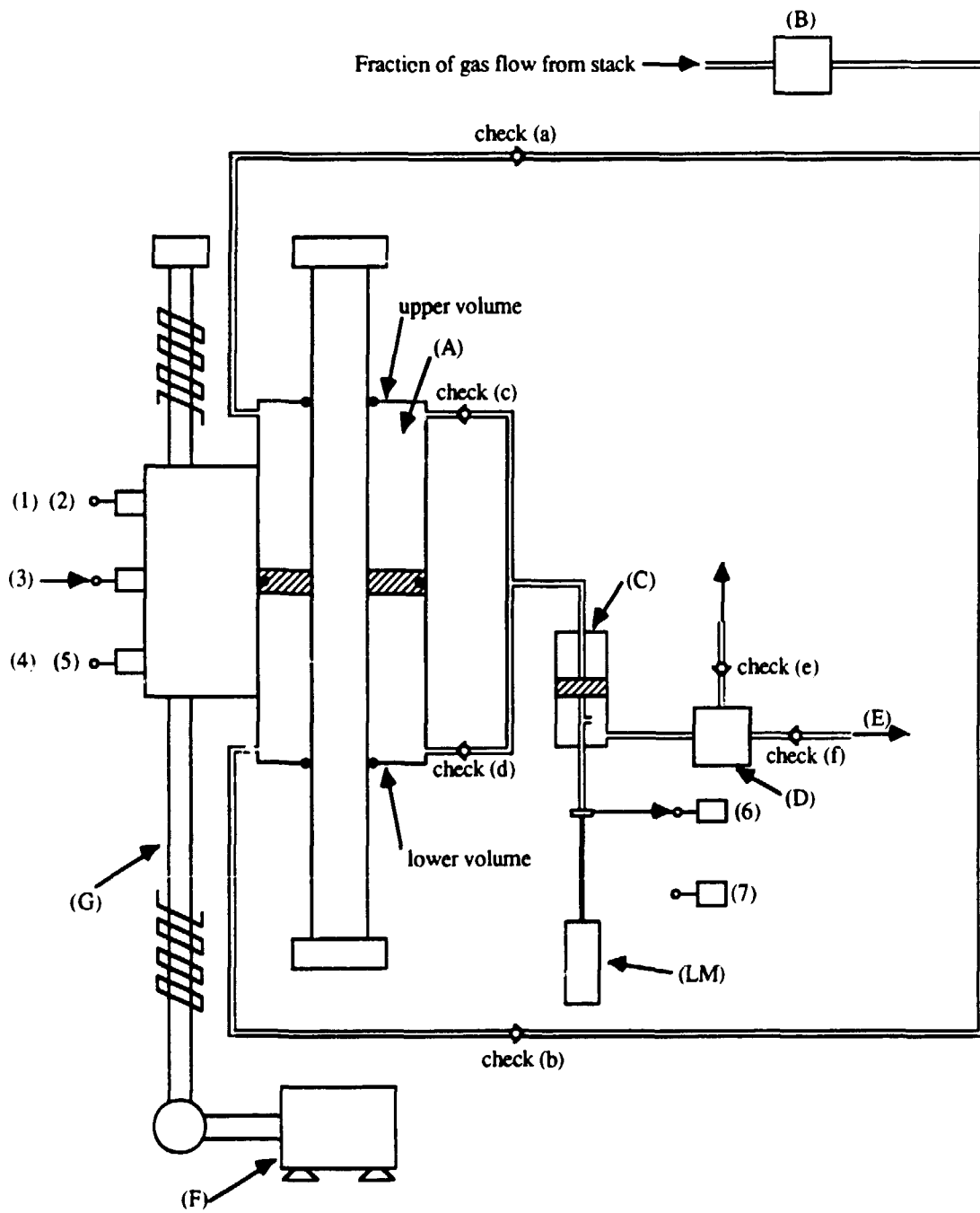


Figure 2 Layout of the stack air sampler

### 3.2.2 Function

The system is shown schematically in figure 2. A single-phase A.C. motor (F) actuates a trapezoidal threaded screw (G) backwards and forwards. A nut on the screw acts as an intermediary in moving the double-acting cylinder forwards and backwards with a length of stroke of maximum 500 mm. The upper and lower parts of the double-acting cylinder are connected to the monitoring system of the stack via a pipe with check valves (check (a) and check (b)) and the particle filter (B). The double-acting cylinder is also connected to a pump consisting of a small pressure cylinder whose piston is actuated by a linear motor (LM). The pump's outlet is affiliated to a three way solenoid valve (D). One of the other two exits of the solenoid valve is connected via check valve (e) to the sample balloon and the other goes out in the surrounding room, via check valve (f).

When the screw has moved the cylinder (A) to the upper end the break-coupling (4) reacts and the motor changes direction. The cylinder will then move downwards with check valve (a) closed and check valve (b) open. Air will be drawn out from the stack monitoring system via check valve (b). At the same time check valve (c) is open, check valve (d) closed, check (e) open and (f) is closed. During this process there is no connection between check valve (f) and the flowing gas since the solenoid valve's gate to check valve (f) is closed. Air will then flow from the upper part of the cylinder through the small pressure cylinder and via the solenoid valve out into the surrounding room.

When the cylinder is about half-way down to the lower end break-coupling (3) is affected. The linear motor, being at one of its ends, will then start driving the piston in the pressure cylinder (C). The solenoid valve will then make sure that the gate to check valve (e) is closed and the gate to check valve (f) is open, resulting in gas flowing from the pressure cylinder into the balloon. As the linear motor and also the piston in the pressure cylinder have reached the other end, the break-coupling (7) is affected, making the linear motor change direction, moving the piston to the starting position. At the same time the solenoid valve is reverted. When the other end is reached the break-coupling (6) is affected. The process filling the lower volume of the cylinder ( ) and emptying the upper one has meanwhile continued and will do so until the bottom end is reached and break-coupling (2) is activated, whereupon the process is repeated. Break-couplings (1) and (5) are safety breakers to check valves (2) and (4).

It takes 13.4 minutes to fill the 5 litres into the cylinder. The speed of the cylinder is then 0.62 mm/s. The linear motor has a speed of 1.7 mm/s and it takes only 27 seconds to transfer the gas volume of the small cylinder to the balloon.

### 3.3 Sample preparation

#### 3.3.1 The carbonatization system

In the carbonatization system a  $^{14}\text{C}$ -free carrier gas is added to the stack air sample and the carbon compounds are converted into sodium carbonate.

##### 3.3.1.1 Construction

The carbonatization system is shown in figure 3. There are two distinguishable parts of the construction: the gas-mixing part and the carbonate formation part. All parts are connected as shown in the figure by 1/4" copper pipes. Valves and fittings are also made of copper. Coupling copper to glass involves Teflon ferrules.

##### 1) The gas-mixing part

The glass tube  $V_1$  (10.5 ml) defines a constant volume of carbon dioxide (99,99 %) taken from a carbon dioxide tube, and is used to add a known amount of non-active carbon dioxide to the air sample whose volume is defined by the glass bubble  $V_2$  (5210 ml). The sample balloon is connected in the way the figure illustrates. The gas amount is measured with a Bourdon pressure gauge with a precision within 1%. When mixing the two gases, the cold finger helps transferring the carbon dioxide close to the glass bubble.

##### 2) The carbonate formation part

The carbonate formation part consists of two Pyrex glass tubes filled with Drierite (diameter 1/2", length 200 mm), one quartz glass tube (diameter 1/4", length 170 mm) filled with a catalyst (a mixture of pellets of PdAl- and PtAl-oxide), a Pyrex tube (diameter 1/4", length 65 mm) containing the Ascarite (20-30 mesh solid sodium hydroxide) and a flow meter. The catalyst's tube is surrounded by an oven which is kept at 600 °C. A vacuum pump is used to draw the gas from the gas-mixing part to the carbonate formation part. The flow through the system is controlled with two regulating valves (i and j in figure 3).

When evacuating the system it is convenient to use the separate copper tube parallel to the carbonate formation line.

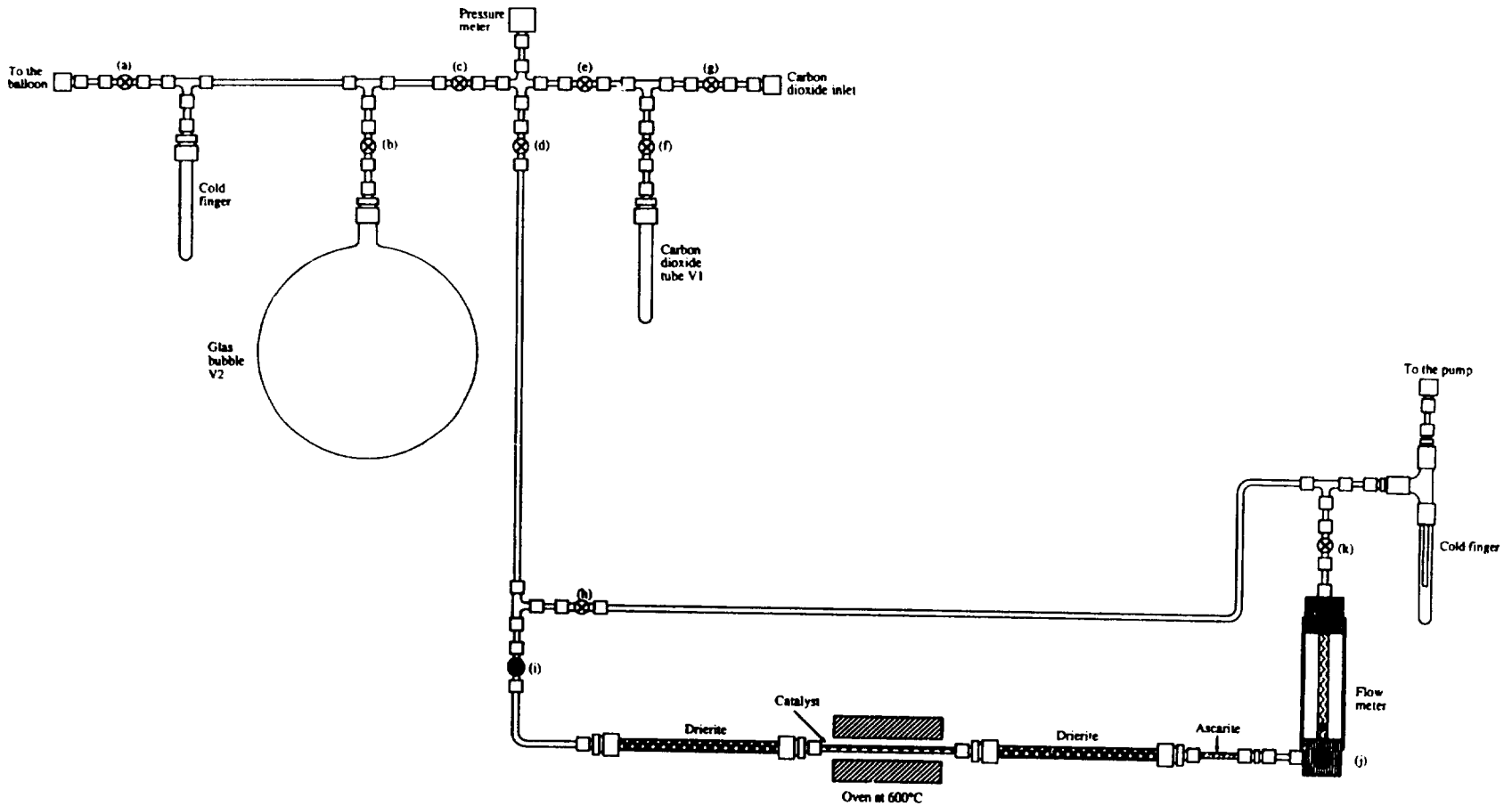


Figure 3 The carbonatization system

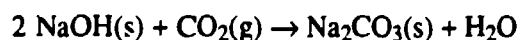


### 3.3.1.2 Function

When the whole system has been evacuated, carbon dioxide is let into V<sub>1</sub>. All the valves except (e), (g) and (f) are closed and the pressure is measured. Closing valves (g) and (f) and opening valves (d) and (h) the copper pipes leading from V<sub>1</sub> will be evacuated.

The balloon is connected to its inlet and with all valves but (a), (b) and (c) closed V<sub>2</sub> will be filled with the gas sample. If the pressure in V<sub>1</sub> is 3.2 times higher than in V<sub>2</sub> the <sup>12</sup>C and <sup>13</sup>C content of the sample will be diluted 20 times (assuming that the air sample contains 330 ppm carbon dioxide). Closing (a) and (b) and opening (d) and (h) the pipes leading from V<sub>2</sub> will be evacuated. A dewar flask filled with liquid nitrogen is placed around the cold finger to the left of V<sub>2</sub> in figure 3. Closing valve (d) and letting (c), (e) and (f) be open, the carbon dioxide will be transferred to the cold trap where it freezes. After closing valve (c) and letting the carbon dioxide evaporate, valve (b) is opened allowing the two gases to mix by diffusion. 30 minutes is considered enough in order to get the gases well mixed.

To draw the gas through the carbonate formation line valve (h) is closed, valves (c), (d) and (k) are opened, and the flow is controlled with the regulating valves (i) and (j). When passing through the heated catalyst, all carbon compounds are oxidised to carbon dioxide. The Ascarite then absorbs only the carbon dioxide in the air sample according to the reaction



while all other gases pass through the Ascarite and are transported away by the vacuum pump. The Drierite tubes dry the gas mixture in order to prevent the Ascarite from absorbing water vapour, which would decrease the Ascarite's efficiency.

Starting with a pressure of 0.5 bar in V<sub>2</sub> the process takes about 6 hours with this construction.

### 3.3.2 The graphitization system

In the graphitization system the sodium carbonate is transferred into graphite, by converting the carbonate to carbon dioxide, and reducing it to graphite over a catalyst. Many processes have been used for elemental carbon preparation, especially for <sup>14</sup>C dating, like piston cylinder graphitization (Bonani et al [13]) and cracking of carbon monoxide (Grootes et al [14]) or acetylene (Beukens et al [15]). Our method is based on

the production of elemental carbon by the catalytic reduction of CO<sub>2</sub> over an iron-group metal powder. Vogel et al [16] were the first to deploy this method for AMS measurements. Since then a number of methods have been suggested to improve this procedure by bringing down the reaction time, for example forced gas circulation (Hut et al [17]) or using a small reaction volume and a higher start pressure (Lowe and Judd [18]).

### 3.3.2.1 Construction

The graphitization system is outlined in figure 4. The system is connected to a mercury diffusion pump backed by a mechanical pump. The liquid nitrogen trap of the diffusion pump also prevents back streaming. The pressure in the evacuated system is below 10<sup>-4</sup> mbar. A good vacuum is needed to avoid cross-contamination.

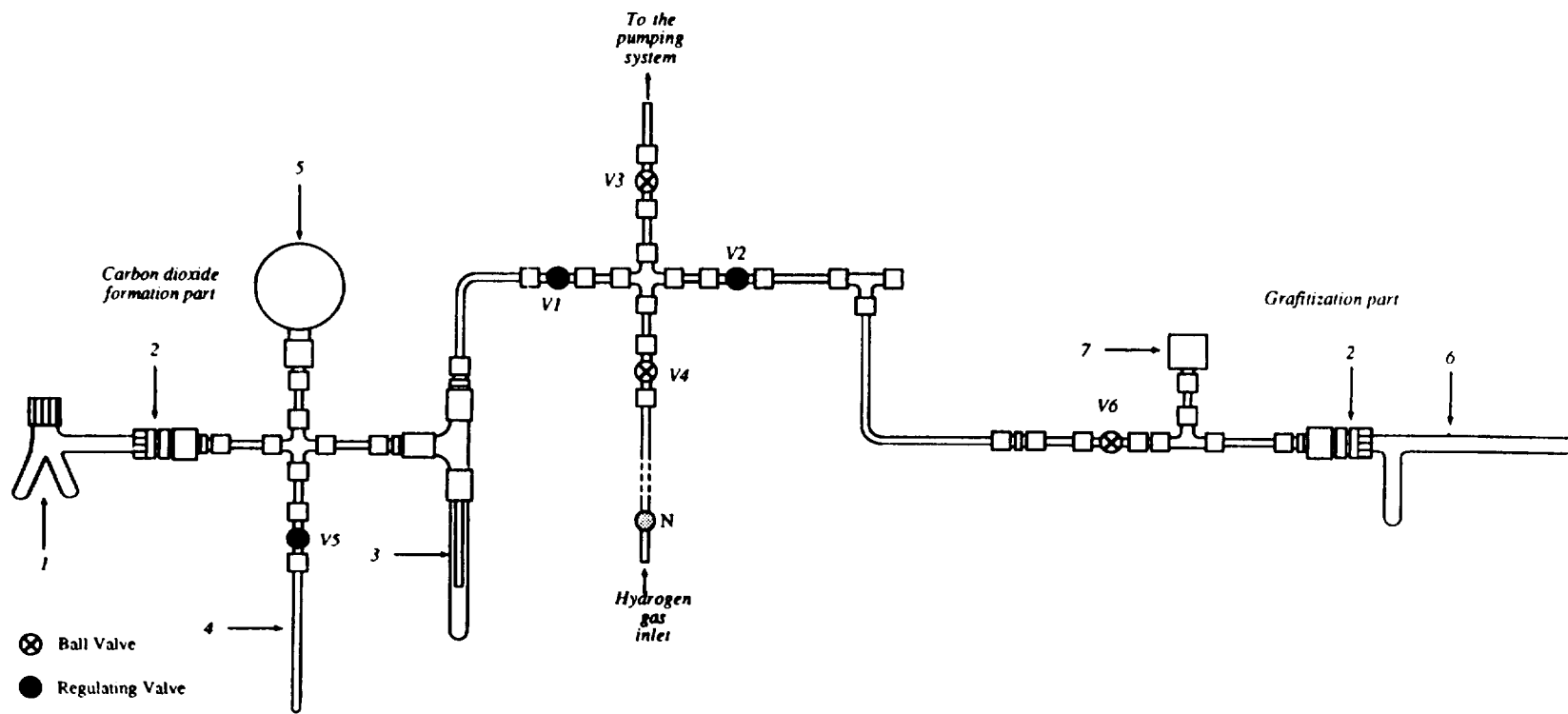
Pure H<sub>2</sub>-gas (99,9997 %) is required for the graphitization process and is led into the system through valve V4. The gas stream is controlled with a needle valve (N) so that the desired pressure is easily reached.

All stainless steel tubing, used to connect different parts of the system, have 6 mm outer diameter.

#### 1) Carbon dioxide formation

Carbon dioxide is produced in the subsystem to the left of valve V1. A three-pipe construction of Pyrex glass (1) is used when the carbon dioxide is released from Ascarite samples and is connected to the system with a 1/2" Cajon O-ring fitting (2). The cold trap (3) is made of 12 mm Pyrex glass tubing fitted to a stainless steel Swagelock Tee. A stainless steel tube runs through the Tee and into the glass tube, cooled by an ethanol-dry ice mixture at a temperature of -78°C.

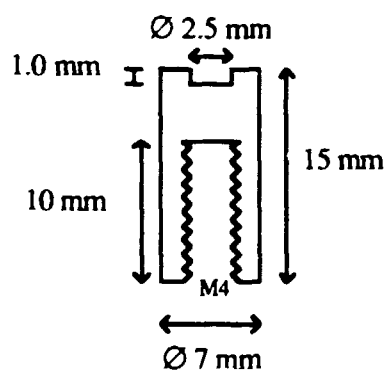
Figure 4 The graphitization system



Below valve V5 in figure 4 a water-filled 6 mm glass-tube (4) can be fitted giving the possibility to bring water vapour into the system (see below). The glass to steel fittings (except the Cajon O-ring) are equipped with Teflon furrrels. The pressure is measured with a Bourdon pressure meter (5) (-1.0 to + 1.5 bar). The volume of the carbon dioxide formation system is approximately 40 ml.

## 2) CO<sub>2</sub> to C conversion

Elemental carbon is produced in the subsystem to the right of valve V6 in figure 4. The CO<sub>2</sub> to C conversion takes place in a two-legged 1/2" quartz tube (6). One leg is used as a cold trap, kept at -78°C by an ethanol-dry ice mixture, absorbing water vapour. The other leg, where the carbon sample is collected, is surrounded by an oven kept at 650°C. Before the graphitization process the catalyst of iron powder (99.9 %, -325 mesh) is placed in the well of a copper piece, shown in figure 5.



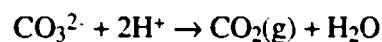
*Figure 5 The copper piece in which the iron powder is placed*

The pressure of CO<sub>2</sub> and H<sub>2</sub> is measured with a Bourdon pressure gauge (7) and recorded continually with a writer. The pressure can also be read with a display monitor. The volume of the graphitization part is approximately 21 ml.

### 3.3.2.2 Function

The Ascarite sample, processed in the carbonatization system, is placed in one of the two legs of the glass tube to the left in figure 4. In the other leg ca 3 ml phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is placed. Phosphoric acid is suitable because of its low vapour pressure.

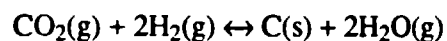
When the whole system is evacuated, and all valves are closed, the phosphoric acid is tipped into the Ascarite. Carbon dioxide will then be emitted according to the reaction:



The cold trap with dry ice in alcohol collects moisture and some pollutions. The small tube with water is used to clean the system: water vapour can fill the system, and then be frozen down, bringing pollutions with it.

When the carbon dioxide forming reaction has stopped, the gas is transferred to the graphitization part by the help of a liquid nitrogen trap. The oven should then already be in position and the horizontal glass leg containing about 10 mg iron powder pressed into the copper probe should have been heated to 650 °C for about 15 minutes. The amount of carbon dioxide is measured by the pressure meter. With the carbon dioxide frozen in the cold trap, hydrogen gas is let into the system. It is suitable to have 3-4 times more hydrogen gas than carbon dioxide. The liquid nitrogen is removed from the cold trap, and is replaced with the ethanol-dry ice mixture, allowing the carbon dioxide to evaporate.

The reaction taking place will be



Since this is an equilibrium process the water vapour must be removed in order to force the process to the right of the reaction (le Chatelier's principle). In fact, the reduction process occurs in several steps. First carbon oxide is formed, then solid carbon. Hydrocarbons may also be formed if the temperature is less than 550°C.

When the reduction is completed the system is evacuated from remaining hydrogen gas. The oven is removed and the heated glass tube is cooled down, whereupon the Fe-C mixture is pressed into the well of the copper probe (figure 5) with a stainless steel piston. The copper piece is then fitted into the ion source of the accelerator. The total amount of carbon is a few milligrams.

It is very important that glass details, the copper probe and the entire system are clean and without pollutions, since pollutions may slow down the reaction dramatically. It is important that oil from the production process of the probes is removed. The reduction time is 1-4 hours, depending on the purity of the system.

### 3.4 The AMS facility

#### 3.4.1 Construction

The AMS facility is based on the Pelletron tandem accelerator in Lund. A detailed description of the Pelletron system is available in Swedish by Hellborg and Håkansson [19] and different parts of the AMS system have been described by Erlandsson et al [20] and Skog et al [21].

The construction of the AMS facility is shown in figure 5. The essential parts of the tandem accelerator system are the injector, the inflection magnet, the accelerator, the analysing magnet, the experimental set-up and the vacuum equipment.

##### 1) The injector

In the injector negative ions are created in a caesium sputtering source of the ANIS type [12] shown in figure 7 and given a certain initial energy. Electrostatic lenses form the ions to a beam, suitable for injection into the accelerator.

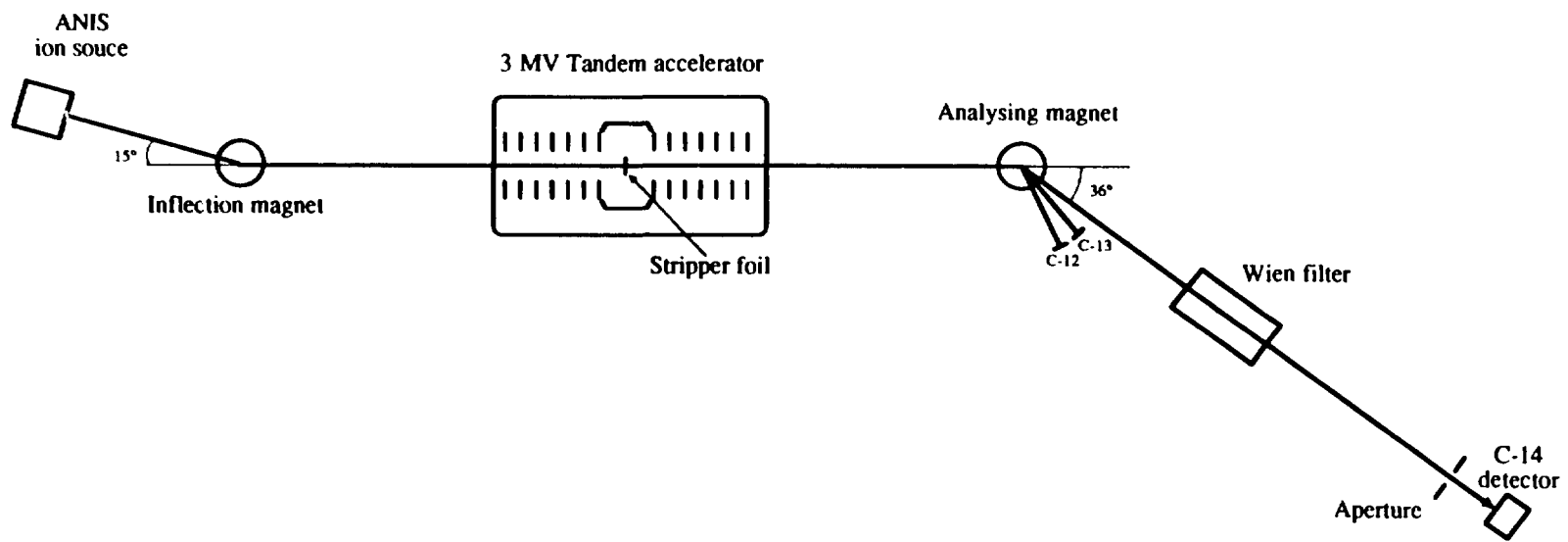
The 15° inflection magnet selects the ion mass that is to be injected into the accelerator.

##### 2) The accelerator

The accelerator consists of a high voltage generator with good voltage stability, an acceleration tube that the beam passes along and a stripper equipment converting the negative ion beam into a positive beam. Different kinds of optical devices situated along the beam path make it possible to vary the position and the shape of the ion beam.

A pressure tank containing SF<sub>6</sub> encloses the accelerator in order to minimise the risk of electrical discharges. Loading the high voltage terminal is done with rotating chains consisting out of metallic cylinders connected with links made of an insulating material. The cylinders are charged through induction and transport the charge to the terminal where it is delivered by contact. In the terminal there is a carbon stripping foil of thickness 2 µg/cm<sup>2</sup>, tearing electrons off the ions when they pass through the foil.

Figure 6 The AMS facility



### 3) Beam analysing equipment

Before the  $^{14}\text{C}$  ions reach the counting equipment they have to be sorted out from a high background. This is done in two steps after the ions have been accelerated. First the beam enters the analysing magnet which sorts out the right mass, energy and charge state and secondly the beam passes through a velocity analyser consisting of a combined electric and magnetic field (a so called Wien filter).

### 4) Experimental set-up

The experimental set-up simply consists of a detector able to count particles and a multichannel analyser to register the counts and the energy of the particles. Two types of charged-particle detectors have been used: a PIPS detector Canberra PD-300 and a windowless Hamamatsu S2744-04 photodiode both with a resolution of 27 keV for 8785 keV  $\alpha$ -particles.

#### 3.4.2 Function

In the injector's ion source (figure 7), containing the copper probe with carbon from the air sample, there is evaporated caesium. A current of 30 - 40 A is sent through the two filaments in the source so that electrons are emitted. A magnetic field forces the electrons to move helix-like resulting in collisions between the electrons and the free caesium atoms. The caesium atoms that are hit can give up an electron and become the positive ion  $\text{Cs}^+$ . The ions can recombine with the free electrons in the chamber or be accelerated towards the probe with the carbon sample, since it acts as a cathode. When the ions bombard the carbon sample sputtering can take place, i. e. positive, neutral and negative carbon ions will be emitted from the surface of the probe.

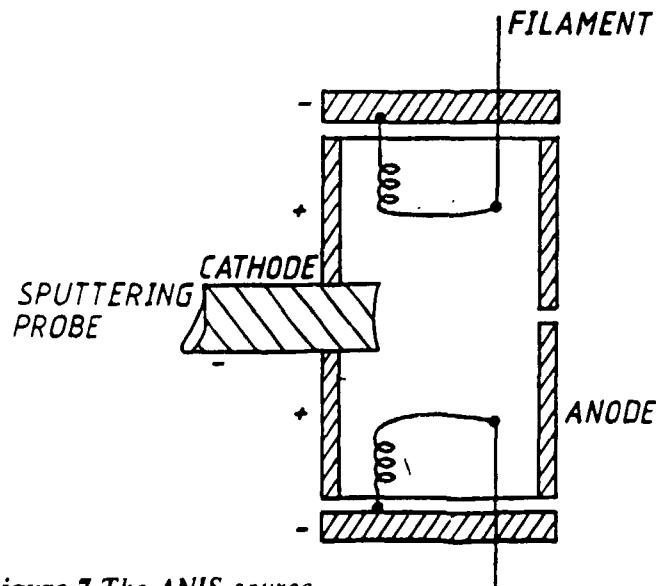


Figure 7 The ANIS source



The ion source is kept at a negative potential of 40 kV relative to ground giving the negative carbon ions an initial energy of 40 keV when they are accelerated into the evacuated beam tube at ground potential. The negative carbon ion current is around 5  $\mu$ A.

The inflection magnet allows only particles with a certain momentum to pass it, so that unwanted ions created in the ion source will be sorted out. The negative ions will then reach the accelerator and be accelerated towards the high voltage terminal at 2.7 MV. Passing through the carbon foil at the terminal, electrons will be torn off resulting in a positive ion beam with ions in different charge states. Repelled by the terminal the now positive particles in the beam will continue to be accelerated to ground and move on towards the analysing magnet. Along the beam tube electrostatic and magnetic lenses are situated, in order to steer and shape the ion beam.

Together with the  $^{14}\text{C}^-$  ions there will be a lot of other mass-14 ions coming out from the ion source such as  $^{12}\text{CH}_2^-$  and  $^{13}\text{CH}^-$ , however not  $^{14}\text{N}^-$  due to its short lifetime. When passing through the carbon stripper foil at the accelerator terminal the molecule ions tend to break up. Molecular ions with charge states 1+ and 2+ have been observed, but no ion with charge states 3+ or higher will survive. Thus to sort out molecular ions only particles with charge state 3+ are allowed to pass the analysing magnet. The distribution of the different charge states is depending on the terminal voltage. It is chosen to 2.7 MV since for carbon the 3+ state is dominating at that voltage.

When the  $\text{C}^{3+}$  ions have passed the analysing magnet the velocity analyser acts as a last filter to get rid of ions that have changed charge state through collisions with rest molecules along the beam tube and thereby managed to slip through the analysing magnet. In the velocity analyser ions with incorrect velocities are bent off in different angles from the beam path leading to the detector. To get rid of the ions moving in angles close to the beam path there is a rectangular aperture just before the detector.

The  $^{13}\text{C}$  content can be measured as a current at a Faraday cup on a beam stop just before the detector system. The number of  $^{14}\text{C}$  atoms is measured during totally 800 seconds by the detector.  $^{13}\text{C}$  and  $^{14}\text{C}$  are measured in a cycle consisting of 30 seconds of  $^{13}\text{C}$  and 200 seconds of  $^{14}\text{C}$ , starting and finishing with  $^{13}\text{C}$ . During the cycle  $^{13}\text{C}$  is measured on a beam stop situated in a chamber after the analysing magnet. In this way the field of the analysing magnet can be constant and only the field of the inflection magnet is scanned in order to measure the intensities of  $^{13}\text{C}$  and  $^{14}\text{C}$ .

#### 4. Calculations

The following calculations are used when determining the  $^{14}\text{C}$  activity concentration of air samples measured at the AMS facility.

The ratio between the abundance of the isotopes  $^{13}\text{C}$  and  $^{14}\text{C}$  is determined by separately measuring the number of  $^{13}\text{C}$  and  $^{14}\text{C}$  atoms. What is actually measured is the number of  $^{14}\text{C}$  atoms entering the detector per second,  $N_{\text{C-14}}$ , while the number of  $^{13}\text{C}$  atoms is measured as a current  $I_{\text{C-13}}$ . When transforming the  $^{13}\text{C}$  current into ions per second,  $N_{\text{C-13}}$ , one gets:

$$N_{\text{C-13}} = \frac{I_{\text{C-13}}}{q \cdot e} \quad (1)$$

where  $q$  is the ion charge state (i. e. 3 in this case since the ions are ionised three times) and  $e$  is the elementary charge.

The amount of mole of  $^{14}\text{C}$  atoms,  $n_{\text{C-14}}$ , in the mixed gas sample is given by:

$$n_{\text{C-14}} = n_{\text{C-13}} \cdot \frac{N_{\text{C-14}}}{N_{\text{C-13}}} \quad (2)$$

All  $^{14}\text{C}$ -atoms are supposed to come from the stack air (volume  $V_2$  and pressure  $p_2$ ), while the contribution to  $n_{\text{C-13}}$ , the amount of mole of  $^{13}\text{C}$  atoms, mainly comes from the carrier gas (volume  $V_1$  and  $p_1$ ) with a minor contribution from the stack air.

To calculate  $n_{\text{C-13}}$  the following relation is used:

$$n = \frac{p V}{R T} \quad (3)$$

where  $n$  is the amount of mole for a certain gas with pressure  $p$ , volume  $V$  and temperature  $T$ .  $R$  is the ideal gas constant. In the  $\text{CO}_2$  gas, with volume  $V_1$  and  $p_1$ , there is 1.1 %  $^{13}\text{CO}_2$ . Eq. (3) therefore gives:

$$n_{\text{C-13, CO}_2 \text{ gas}} = 1.1 \% \cdot \frac{p_1 V_1}{R T} \quad (4)$$

In the stack air sample, with volume  $V_2$  and pressure  $p_2$ , there is about 330 ppm  $\text{CO}_2$  of which 1.1 % is  $^{13}\text{CO}_2$ . Eq. (3) therefore gives:

$$n_{C-13, \text{ stack sample}} = 330 \text{ ppm} \cdot 1.1 \% \cdot \frac{p_2 V_2}{R T} \quad (5)$$

The total amount of mole of  $^{13}\text{C}$  atoms in the mixed gas is therefore obtained from equations (4) and (5):

$$n_{C-13} = n_{C-13, \text{ CO}_2 \text{ gas}} + n_{C-13, \text{ stack sample}} \quad (6)$$

Transforming  $p_2$  to normal pressure  $p_{\text{norm}}$ , the volume  $V_{\text{norm}}$  of the gas will be:

$$V_{\text{norm}} = \frac{p_2 V_2}{p_{\text{norm}}} \quad (7)$$

Consequently the amount of mole of  $^{14}\text{C}$  atoms, in the stack air sample per gas volume at normal pressure, is obtained by:

$$n_{C-14, \text{ normal pressure}} = \frac{n_{C-14}}{V_{\text{norm}}} \quad (8)$$

Finally, the activity concentration  $A_{C-14}$  for the  $^{14}\text{C}$  atoms is obtained by:

$$A_{C-14} = n_{C-14, \text{ normal pressure}} \cdot \lambda \cdot N_A \quad (9)$$

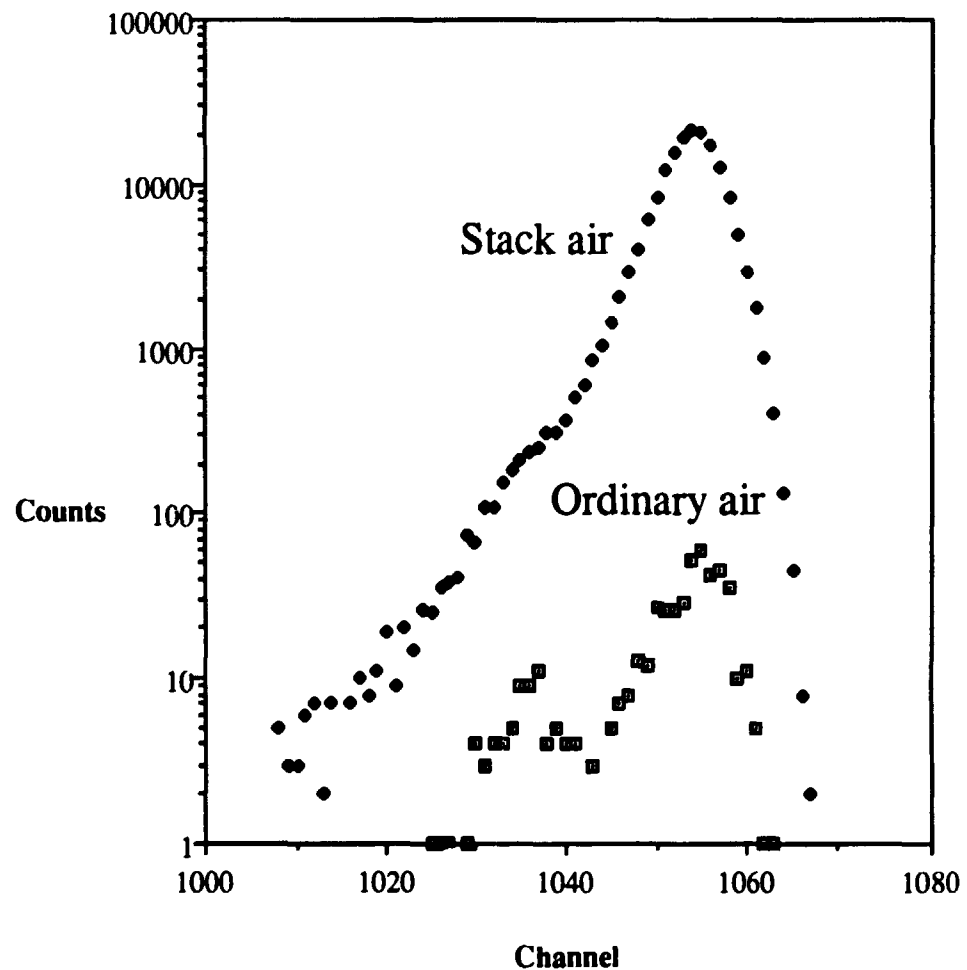
where  $\lambda = \ln 2/T_{1/2}$  is the decay constant for  $^{14}\text{C}$  and  $N_A$  is Avogadro's constant. By using suitable units for the different quantities ( $n_{C-14, \text{ normal pressure}}$  in mole/m<sup>3</sup>,  $\lambda$  in s<sup>-1</sup> and  $N_A$  in atoms/mole)  $A_{C-14}$  will be obtained in Bq/m<sup>3</sup>.

## 5. Results

The stack air samplers have turned out to be reliable, and four of them have so far served continuously for more than 9000 hours each without any fault. The sample preparation system has also been found to work well. An important detail about the graphitization system is that the glass parts and copper pieces are clean. Traces of oil used when producing the probes slow down the reduction rate enormously.

An example of a typical  $^{14}\text{C}$  spectrum from the stack air is shown in figure 8. Also shown in this figure is a spectrum from ordinary air containing about 340 ppm of  $\text{CO}_2$ . Both spectra are obtained with the Hamamatsu S2744-04 photo diode as the particle detector. The left top in the ordinary air peak is probably nitrogen that has passed through

the inflection magnet as tails of  $^{14}\text{NH}^-$ . In the stripping process  $^{14}\text{N}^{3+}$  will appear, having only slightly different energy (and velocity) than  $^{14}\text{C}^{3+}$  but the same mass and charge state, implying that nitrogen will pass both the analysing magnet and the Wien filter and reach the detector.



*Figure 8 An example of two  $^{14}\text{C}$  spectra*

Within this project about 10 samples both from the Ringhals plant and from the Forsmark plant have been processed and measured (tables 2 and 3). Some of the gas samples from Ringhals have also been processed in the carbonatization system without the heated catalyst, meaning that only the  $^{14}\text{C}$  activity of the  $\text{CO}_2$  in the stack air has been measured.

Period	CO <sub>2</sub> activity (Bq/m <sup>3</sup> )	Total <sup>14</sup> C activity (Bq/m <sup>3</sup> )
911021-911101 (v 43-45)	25 ± 4	39 ± 6
911104-911118 (v 45-47)	8 ± 1.2	25 ± 4
911118-911202 (v 47-49)	2 ± 0.3	5 ± 0.8
911202-911216 (v 49-51)	16 ± 2	51 ± 8
911216-911230 (v 51-1)	42 ± 6	128 ± 19

**Table 2** The <sup>14</sup>C activity in stack gas from the Ringhals reactor number 4.

Period	Total <sup>14</sup> C activity (Bq/m <sup>3</sup> )
911203-911217 (v 48-51)	80 ± 12
911217-920107 (v 51-2)	125 ± 19
920107-920128 (v 2-5)	80 ± 12
920128-920210 (v 5-7)	118 ± 18
920210-920224 (v 7-9)	74 ± 11

**Table 3** The <sup>14</sup>C activity in stack gas from the Forsmark reactor number 1.

As seen in tables 2 and 3 the activity concentration in Ringhals (PWR) varies between 5 and 128 Bq/m<sup>3</sup> and at Forsmark (BWR) the activity concentration varies between 74 and 125 Bq/m<sup>3</sup>.

Hesböl and Gebert [9] have measured the <sup>14</sup>C activity concentration from Ringhals reactor no 1, a BWR, with liquid scintillation counting. 1110 litres of stack gas was collected and was found to contain 108 Bq/m<sup>3</sup>, which is well in line with the AMS measurements.

## 6. Error estimates

Of the constants and variables introduced in the calculations above the measured volumes and pressures have uncertainties < 5%. The CO<sub>2</sub> concentration in the stack gas may vary, but the adding of <sup>14</sup>C-free CO<sub>2</sub> carrier implies that even very large variations (50 %) in the CO<sub>2</sub> concentration change the result with only about 5-10 %. Normal variations in the CO<sub>2</sub> concentration are < 10 %, which would introduce an error of around 1-2 %. The carbon dioxide concentration in the stack gas has been measured by gas chromatography for one sample of Ringhals air and was found to be 338 ppm as expected from ordinary air. Furthermore, the gas sample contained 1.6 ppm CH<sub>4</sub>, and there were traces of CO.

The stable isotopic composition of the mixed gas samples (the carrier gas plus the carbon compounds of the collected air samples) processed in the carbonatization system has been investigated using conventional mass spectrometry. δ<sup>13</sup>C-values have been measured to be -26.7‰ from PDB (a standard) for one of the Ringhals samples and -27.5‰ from PDB for a home-made active standard. δ<sup>13</sup>C is defined as:

$$\delta^{13}\text{C} = \left[ \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{PDB}}}{(^{13}\text{C}/^{12}\text{C})_{\text{PDB}}} \right] \times 10^3\text{‰}$$

The PDB standard has a <sup>13</sup>C/<sup>12</sup>C ratio of 1.12372 ‰ (Craig [22]), giving a <sup>13</sup>C/<sup>12</sup>C ratio of 1.093 ‰ for the two investigated samples. The isotopic fractionation introduced by the graphitization procedure and by the accelerator has not been measured. However, AMS-measurements of the oxalic acid standard (see below) which has been processed in the graphitization system in the same way as the other samples show a count rate close to the theoretical expected values. Thus, the <sup>13</sup>C/<sup>12</sup>C ratio of 1.1 ‰ used in the calculations seems to be justified.

The <sup>13</sup>C current is the variable which is exposed to the largest variations, but according to our experience the introduced error is only about 10 %. The efficiency of the catalyst in the carbonatization system is 95-100 %, but has only been verified for large amounts of methane. This is not necessarily the case when having very small concentrations of hydrocarbons. To improve the oxidation a carrier of methane can be added to the stack gas, but Hesböl and Gebert [9] mention that the adding of methane hardly shows any improvement in efficiency.

To check the reproducibility of the system standard samples have been measured. Repeated measurements of the <sup>14</sup>C/<sup>13</sup>C ratio for an oxalic acid from NBS (National Bureau of Standards) have given a distribution of measured values of ±12 %. The

deviation of the mean value from the theoretical value is around 3 %. A home-made active standard has a distribution of measured  $^{14}\text{C}/^{13}\text{C}$  ratios of  $\pm 13$  % for the same measuring period. These samples are only processed in the graphitization system and not in the carbonatization system. To check the over all reproducibility of the processing and measuring system two ion source samples from the same gas sample, each processed through the whole system, have been measured on, giving 2.02 and 2.26 Bq/m<sup>3</sup> respectively. Samples of anthracite (old charcoal without  $^{14}\text{C}$ ) have also been measured to ensure that the background of the accelerator system does not introduce any considerable errors in the  $^{14}\text{C}$  measurements.

Based on the error estimates the uncertainties in the given activity concentrations are  $\pm 15$  %. Publications on other methods have reported errors of  $\pm 15$  % [6] and  $\pm 10$  % [10].

## 7. Conclusions

With the AMS method we can deal with the carbon-extraction in the laboratory with well defined volumes and air flows. AMS has several advantages over the radiometrical methods. It requires only a few litres of gas per sample, which is 100-1000 times less compared to the radiometrical methods. By counting the number of  $^{14}\text{C}$  atoms instead of measuring their activity, the problem with the presence of other far more active  $\beta$ - and  $\gamma$ -emitters in the gas sample is avoided. The sample preparation time is about the same for the different methods, but the measuring time with AMS, about 20 minutes per sample, is considerably shorter than when using radiometrical methods, which demand several hours per sample.

The adding of pure  $\text{CO}_2$  to the air sample makes one independent of also rather large  $\text{CO}_2$  variations in the ordinary air (330 ppm). The range of the activity concentrations which can be determined with this method is from below natural atmospheric levels to several 1000's of  $\text{Bq/m}^3$ .

The integrity of this method is high. The analyse of the sampled air is made outside the nuclear power plant. It is easy to seal the mechanism of the stack air sampler and monitor the time the sampler has been working. It is not necessary to sample over such a long time as a fortnight. Samples of between 5 and 10 litres can be obtained in a small balloon within 10 minutes and sent for analyse.

In conclusion a method to measure the concentration of  $^{14}\text{C}$  in stack gases from nuclear power plants by AMS has been developed and has been demonstrated to be useful.



## 8. References

- [1] I. Levin, B. Kromer, M. Barabas and K.O. Münnich: *Environmental distribution and long-term dispersion of reactor  $^{14}\text{C}$  around two German nuclear power plants*, Health Physics 54, 2 (1988) 149-156
- [2] H.H. Loosli and H. Oeschger:  *$^{14}\text{C}$  in the environment of Swiss nuclear installations*, Radiocarbon 31, 3 (1989) 747-753
- [3] M. McCartney, M.S. Baxter and K. McKay: *Global and local effects of  $^{14}\text{C}$  discharges from the nuclear fuel cycle*, Radiocarbon 28, 2A (1986) 634-643
- [4] B. Obelic, I. Krajcar-Bronic, D. Srdoc and N. Horvatincic: *Environmental  $^{14}\text{C}$  levels around the 632 MWe nuclear power plant Krsko in Yugoslavia*, Radiocarbon 28, 2A (1986) 644-648
- [5] K. Stenström, B. Erlandsson, R. Hellborg, K. Håkansson, G. Skog and A. Wiebert: *Measurement of the  $^{14}\text{C}$  concentration in the stack air of two Swedish nuclear power plants by accelerator mass spectrometry. A one year study of a PWR in Ringhals and a BWR in Forsmark.*, LUNFD6/(NFFR-3062)/1-25/(1993)
- [6] M. Snellman: *Sampling and monitoring of carbon-14 in gaseous effluents from nuclear facilities - a literature survey*, Research report, Project SSI P 498.88 (1988)
- [7] D.W. Hayes and K.W. MacMurdo: *Carbon-14 production by the nuclear industry*, Health Physics 32, (1977) 215-219
- [8] E. Hertelendi, G. Uchrin and P. Ormai:  *$^{14}\text{C}$  release in various chemical forms with gaseous effluents from the Paks nuclear power plant*, Radiocarbon 31, 3 (1989) 754-761
- [9] R. Hesböl and G. Gebert: *Mätning av kol-14 utsläpp från kärnkraftverk*, Studsvik/NW-82/327 (1982) (in Swedish)
- [10] C. Kunz: *Carbon-14 discharge at three light-water reactors*, Health Physics 49, 1 (1985) 23-25

- [11] M. Tschurlovits et al: *A comparison of different counting methods for determination of  $^{14}\text{CO}_2$  in air*, Atomkernenergie Kerntechnik Bd 40, 4 (1982) 267-269
- [12] P. Tykesson, H.H. Andersen and J. Heinemeier: *Further investigations of ANIS (The Aarhus Negative-Ion Source)*, IEEE Trans. NS-23 (2) (1976) 1104
- [13] G. Bonani, R. Balzer, H. Hofmann, E. Morenzoni, M. Nessi, M. Suter and W. Wölfi: *Properties of milligram size samples prepared for AMS  $^{14}\text{C}$ -dating at ETH*, Nucl. Instr. and Meth. B5 (1984) 284-288
- [14] P.M. Grootes, M. Stuvier, G.W. Farwell, T.P. Schaad and F.H. Schmidt: *Enrichment of  $^{14}\text{C}$  and sample preparation for beta and ion counting*, Radiocarbon 22, 2 (1980) 487-500
- [15] R.P. Beukens and H.W. Lee: *The production of small carbon samples by re-dissociation of acetylene*, Proc. Symp. on AMS, Argonne (1981) 416-425
- [16] J.S. Vogel et al: *Performance of catalytically condensed carbon for use in accelerator mass spectrometry*, Nucl. Instr. and Meth. B5 (1984) 289-293
- [17] G. Hut et al: *Fast and complete  $\text{CO}_2$ -to-graphite conversion for  $^{14}\text{C}$  accelerator mass spectrometry*, Radiocarbon 28, 2A (1986) 186-190
- [18] D.C. Lowe and W.J. Judd: *Graphite target preparation for radiocarbon dating by accelerator mass spectrometry*, Nucl. Instr. and Meth. B28 (1987) 113-116
- [19] R. Hellborg and K. Håkansson: *Pelletronacceleratorn i Lund*, Internal Report (in Swedish), LUNFD6/(NFFR-3026)/1-294 (1978)
- [20] B. Erlandsson, R. Hellborg, K. Håkansson, G. Skog and B. Bjurman: *Measurements of  $^{14}\text{C}$  from nuclear power plants with the AMS technique*, Nucl. Instr. and Meth. B68 (1992) 309-312
- [21] G. Skog, R. Hellborg and B. Erlandsson: *Accelerator Mass Spectrometry at the Lund Pelletron Accelerator*, Radiocarbon in press

- [22] H. Craig: *Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide*,  
Geochim et Cosmochim 12 (1957) 133-149