

## SAMPLE PREPARATION IN THE GLIWICE RADIOCARBON LABORATORY FOR AMS $^{14}\text{C}$ DATING OF SEDIMENTS

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**Abstract.** The Accelerator Mass Spectrometry has been used in  $^{14}\text{C}$  dating for several years. The  $^{14}\text{C}$  concentration is measured in graphite target. In the Gliwice Radiocarbon Laboratory a system to produce graphite targets has been built. This system will be used for  $^{14}\text{C}$  dating of terrestrial plant and zooplankton macrofossils in lake sediments, and later, in routine  $^{14}\text{C}$  dating of small samples.



### 1. INTRODUCTION

In radiocarbon dating  $^{14}\text{C}$  concentration is measured in samples containing carbon. Beta radiation of that isotope is routinely detected using gas counters and liquid scintillator spectrometers. Another possibility of  $^{14}\text{C}$  detection is Accelerator Mass Spectrometry. It has developed since the 80's. The idea of this technique is direct counting of  $^{14}\text{C}$  atoms. An advantage of this method is a small mass of samples (a few mg) and a possibility to measure much more samples per year than in other methods. Despite the high costs of building and later exploitation of the AMS facility, this technique is being used now for dating various types of samples (bones, sediments, macrofossils, *foraminifera*) in many laboratories. In Poland, the accelerator technique has been used for dating terrestrial plant macrofossils from Lake Gościąg and Lake Perespiłno (Goslar, 1995, 1996 and 1999).

In the AMS technique the  $^{14}\text{C}$  concentration is measured in graphite prepared from gaseous  $\text{CO}_2$  obtained by combustion of the sample. Graphite is pressed into a target of a few millimetres in diameter, which is placed in ion source of accelerator. Carbon ions ( $^{12}\text{C}^3$ ,  $^{13}\text{C}^3$  and  $^{14}\text{C}^3$ ) are produced in source in process of sputtering the graphite target with caesium beam (Benett *et al.*, 1977). In Europe, this technique is used in a few laboratories (Arnold *et al.*, 1989; Bennett *et al.*; 1977; Nadeau *et al.*, 1997; van der Plicht *et al.*, 1995; Possnert *et al.*, 1990; Rom *et al.*, 1998). Graphite targets are produced in more laboratories. Also in the Gliwice Radiocarbon Laboratory the system to produce graphite targets has been built. It contains lines for sample preparation, sample combustion,  $\text{CO}_2$  purification, production of graphite from gaseous samples and pressing it into the target.

The line for graphitisation will be used in dating terrestrial and marine plant macrofossils and zooplankton. A purpose of this work is to study a problem of representativeness of macrofossils in absolute dating of lake sediments by the radiocarbon method. Results of radiocarbon dating of samples from Lake Perespiłno suggest a possibility of redeposition of terrestrial macrofossils (Goslar, 1999) which limits reliability of such dates. A Line for graphitisation will be later used in routine dating.

Authors of this paper have taken advantage from their visits in the Laboratoire des Sciences du Climat et de l'Environnement in Gif-sur-Yvette, France (Arnold, 1989) and in the Leibniz-Labor für Alterbestimmung in Kiel, Germany (Nadeau *et al.*, 1997, 1998). The graphite targets will be sent for AMS measurement in the Laboratory in Kiel.

### 2. SAMPLE PRETREATMENT

Terrestrial macrofossils are pretreated using the AAA method (Acid-Alkali-Acid, de Jong *et al.*, 1986). In this method during the first treatment of sample with HCl solution carbonate contamination is removed, and treatment with NaOH solution removes humid acids. Second treatment with HCl solution removes atmospheric carbon, which could be absorbed during treatment of the sample with NaOH.

In **Table 1** are shown different methods of samples pretreatment used in the Laboratory in Gif-sur-Yvette and Laboratory in Kiel. Both laboratories have different methods of pretreatment. Probably the most important difference in pretreatment is temperature and duration of it. In Laboratory in Gif-sur-Yvette samples are treated in reagents at higher temperatures than in Kiel. In higher temperatures acid can easier react with carbonates and the time of treatment can be shorter.

Preparation is performed in closed vials to avoid sample evaporation during heating and to minimise contact of the sample with atmospheric CO<sub>2</sub>. In Kiel Laboratory samples are treated with HCl and NaOH solutions in room temperatures in open vials. In this condition reaction proceeds slowly, the preparation time is longer, and risk of sample contamination with atmospheric CO<sub>2</sub> is bigger.

In Gif-sur-Yvette after each step of pretreatment the sample is washed to pH neutral by adding portions of distilled water and drawing away the solution with glass micropipette. During washing the sample with distilled water in Kiel the solution in each step is carefully poured out. In the Gif-sur-Yvette Laboratory, small samples are frozen in liquid nitrogen on the end of a steel stick and then carried into a quartz tube. In this tube the sample is dried. In Kiel Laboratory small samples are carried to a quartz tube with water using pipette, and then dried, while bigger samples are carried into the tubes with pincette.

The sample preparation used in Gif-sur-Yvette seems to be more effective and safe. That is why in the Gliwice Laboratory similar sample preparation will be used.

### 3. COMBUSTION

Dried sample is placed in a quartz tube baked earlier in 900 °C through 3h. To the sample copper oxide is added, which is the source of oxygen needed for combustion, and silver wool, which is needed to remove the

gaseous sulphur and chlorine compounds. In Kiel Laboratory CuO is baked in atmospheric air before adding to the sample (Table 2). In the future, baking of CuO in a stream of pure oxygen to avoid contamination with CO<sub>2</sub> from the air (P. Grootes, personal information) is planned. During fast cooling of CuO, strong absorption of atmospheric CO<sub>2</sub> occurs.

CO<sub>2</sub> absorption in CuO granules can happen during cooling of hot CuO in the air and during admitting the air after heating CuO in vacuum. In Gif-sur-Yvette Laboratory, CuO granules are preheated in oxygen and the danger of absorption during the cooling is avoided, but one can expect contamination of CuO during the admission of air after heating CuO and Ag in vacuum directly before adding them to the sample.

Mass of the sample needed to obtain adequate amount of graphite is measured in Kiel before combustion. In Gif-sur-Yvette, the whole sample is converted into graphite and if the amount of graphite is sufficient, two graphite targets are made.

In Kiel Laboratory, for sample combustion a 9 mm quartz tube (in diameter) is used, inside which a 6 mm tube is placed, which contains the sample with CuO and Ag. Afterwards all is connected to the vacuum line (Fig. 1A), pumped out and sealed under vacuum. Then the sample is combusted in muffle oven in temperature 900 °C for a few hours. In Gif-sur-Yvette one quartz tube (9 mm) is used for combustion.

In Kiel, the samples were primarily placed directly in tubes  $\phi=9$  mm. But several accidents with cracking

Table 1. Comparison of sample preparation procedures for <sup>14</sup>C dating with the AMS technique.

Gif-sur-Yvette	Kiel
Preparation in small (ca. 20 cm <sup>3</sup> ) closed vials	Preparation in big (> 100 cm <sup>3</sup> ) open vials
Preparation steps: Treatment of sample with 0,5 M HCl in temp. 50 °C, in water bath, 2 h Washing to pH neutral Treatment of sample with 0,1 M NaOH in room temp., 2 h Washing to pH neutral Treatment of sample with 0,5 M HCl in temp. 50 °C in water bath, 2 h Solution pull off with pipette Drying of the sample	Preparation steps: Treatment of sample with 1% HCl in room temp., 24 h Washing to pH neutral, sample stored in neutral solution by 24 h Treatment of sample with 1% NaOH, in room temp., 24 h Washing to pH neutral, sample stored in neutral solution by 24 h Treatment sample with 1% HCl, in room temp., 24 h Solution outpouring Drying of the sample

Table 2. Comparison of sample combustion processes for AMS <sup>14</sup>C dating.

Gif-sur-Yvette	Kiel
CuO heating (portion for several tens samples) in oxide stream in quartz tube, temp. 800°C	CuO heating (portion for several tens samples) in the air in muffle oven, temp. 800-900°C
	Ag heating in the air in muffle oven, temp. 800-900°C
Amount of CuO and Ag: 0.2 g CuO for sample ca. 0.1 g Ag for sample	Amount of CuO and Ag: 1 g CuO for sample 150 mg Ag for sample
CuO and Ag heating in vacuum in 800°C during 30 min	
Sample heating with CuO and Ag in 100°C during 10 min in vacuum, sealing the tube (the whole placed in single quartz tube $\phi$ 9 mm)	Pumping the sample, CuO and Ag during ca. 12 h, sealing the tube (the whole placed in double quartz tube, $\phi$ 6 mm and $\phi$ 9 mm)
Combustion: quartz tubes placed in muffle oven in 850°C during 6 h	Combustion: quartz tubes placed in muffle oven in 900°C during 2 h

tubes in places of closer contact of CuO and sample with the tube walls occurred. There were not such accidents in Gif-sur-Yvette, probably because the amount of CuO is smaller, and the pressure during combustion inside the quartz tube is lower.

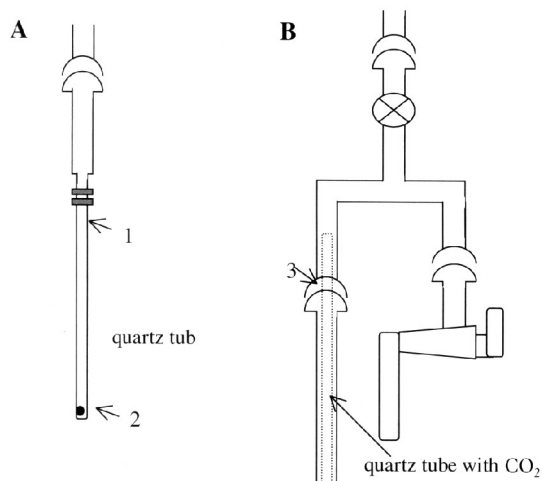


Fig. 1. (A) Line for sealing quartz tubes and (B) for cracking the tubes and purification of CO<sub>2</sub>. 1 – point of sealing the quartz tube; 2 – sample + CuO + Ag; 3 – point of cracking the quartz tube.

In the Gliwice Radiocarbon Laboratory the experience from both laboratories (Laboratory in Gif-sur-Yvette and Laboratory in Kiel) is used. Initial heating of CuO and Ag is performed in oxygen stream. There is no heating of CuO and Ag in vacuum to avoid absorption of CO<sub>2</sub>.

Sample is combusted in single quartz tube (9mm). When using the inner quartz tube, like in the Kiel Laboratory, it is necessary to keep clean both the inner and outer surfaces of the tube (6 mm). This condition is troublesome to fulfil. Samples are combusted in muffle oven in temperature 900 °C for 3 hours.

#### 4. CO<sub>2</sub> PURIFICATION

Quartz tubes with gaseous sample, after cooling, are cracked under vacuum and CO<sub>2</sub> is purified. In Kiel Laboratory, for cracking the tubes ball joints are used (Fig. 1B and Table 3). Earlier incised tube is placed in one arm of the set for cracking tubes, which is cut off from the rest of the line with a cock. After pumping to high vacuum the tube is cracked. CO<sub>2</sub> is collected in glass vial with a cock, and in the arm with the ball joint water vapour is collected in a mixture of dry ice and alcohol. The advantage of this method is a possibility of simultaneous purification of CO<sub>2</sub> samples in several independent sets.

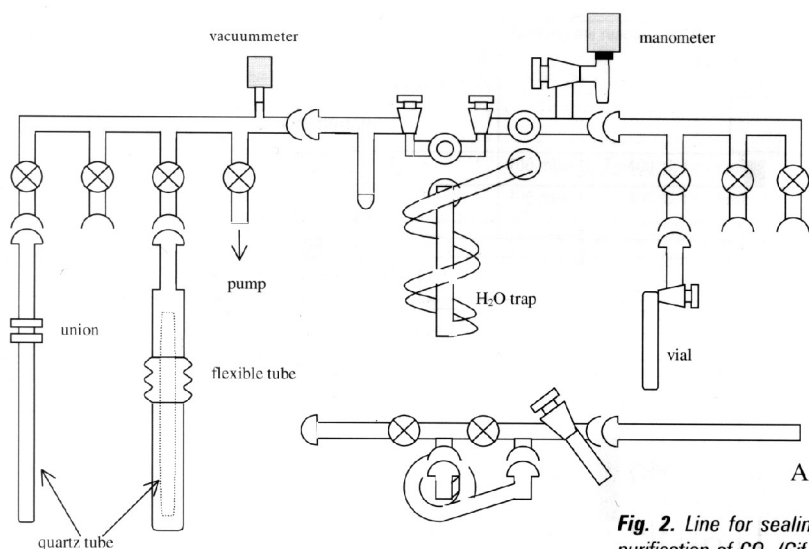


Fig. 2. Line for sealing quartz tubes, cracking the tubes and purification of CO<sub>2</sub> (Gif-sur-Yvette). A – top view of a part of the equipment.

Table 3. Comparison of procedures of CO<sub>2</sub> liberation and purification for <sup>14</sup>C dating by the AMS method.

Gif-sur-Yvette	Kiel
Cracking the tube inside a flexible tube	Cracking the tube inside ball joint
No possibility of purification a few CO <sub>2</sub> samples at one time (Fig. 2)	Possibility of simultaneous purification of CO <sub>2</sub> samples in several independent sets (Fig. 1B)
Measurement of CO <sub>2</sub> amount in a specified volume (Fig. 2)	No measurement of the CO <sub>2</sub> amount

In Gif-sur-Yvette Laboratory the quartz tube is cracked inside flexible tube. After freezing of water vapour, CO<sub>2</sub> is collected in glass vial with a cock. In this system, CO<sub>2</sub> is passed through the whole line, what precludes purification of several samples at one time.

Scheme of a line for liberation and purification of CO<sub>2</sub> in the Gliwice Radiocarbon Laboratory is shown in Fig. 3. In this design has been taken advantages of system construction in Kiel. In this line there is a small reservoir for measuring the CO<sub>2</sub> amount, and two cocks with a small volume in between, used for subtracting an excess of CO<sub>2</sub>. Measured amount of CO<sub>2</sub> is collected in a glass reservoir with a cock.

### 5. GRAPHITISATION

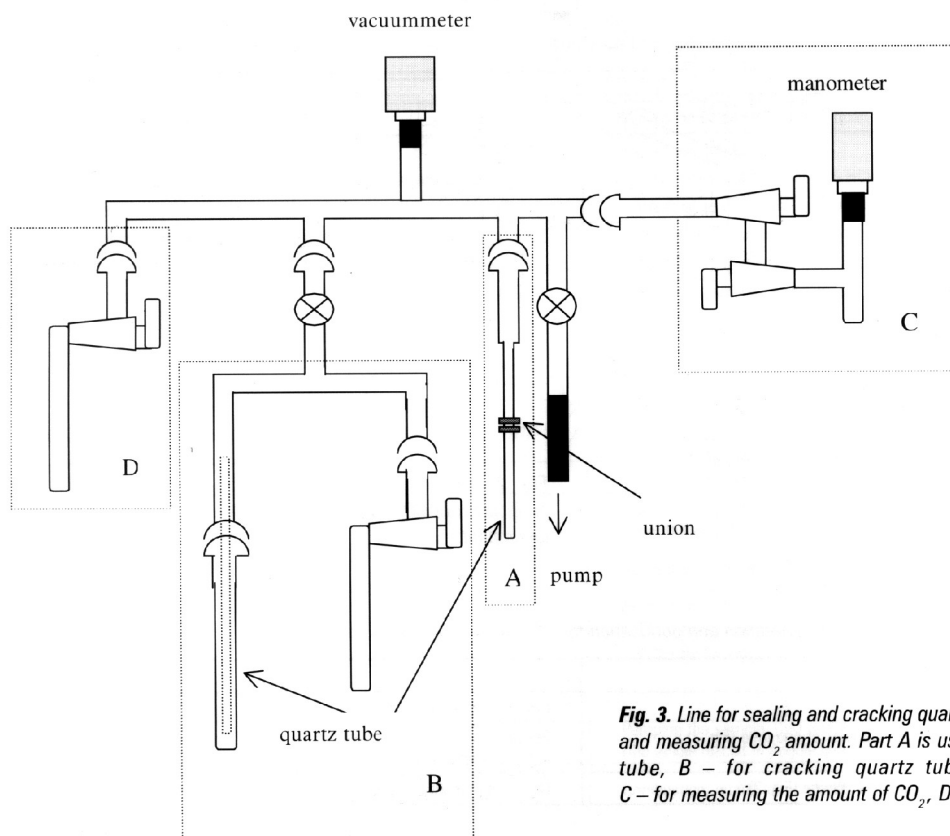
The aim of graphitisation is to produce graphite targets from samples of a few milligrams in weight. Graphite is formed during CO<sub>2</sub> reduction in hydrogen at high temperature. This reaction proceeds on iron powder (Fe) which is a catalyst of this reaction. Weighted portion of Fe is placed in quartz tube horizontally fixed in the reactor (Fig. 4). CO<sub>2</sub> is frozen in the reactor and hydrogen is introduced in an excess of 20%. After defreezing of CO<sub>2</sub> the reduction begins. During reaction H<sub>2</sub>O<sub>gas</sub> and graphite arises, which deposit on iron powder. To maintain this reaction the pressure of water vapour must be kept small. Water vapour is continuously removed by freezing in mixture of dry ice and alcohol. The progress of reaction is continuously moni-

tored by measuring pressure in the reactor. Searching for the best temperature of reaction was made e.g. in Lunds University in Sweden (Stenström *et al.*, 1994), indicating the best temperature for this reaction of ca. 600°C (Table 4).

General scheme of line for graphitisation (Fig. 4) is similar to that in the Kiel and Gif-sur-Yvette laboratories. Different is the amount of Fe used in the reduction. In Kiel the mass of Fe is constant (2 mg), and CO<sub>2</sub> portion corresponding to 1 mg of carbon is separated before the reaction. If the amount of CO<sub>2</sub> corresponds to <1 mg C and >0,5 mg C, the Fe mass is proportionally lower. If the CO<sub>2</sub> amount is less than 0,5 mg the Fe mass is 1 mg. In Gif-sur-Yvette from one sample two targets are prepared. Because of that the whole sample is used, and the amount of Fe is assorted proportionally to the mass of the sample. Fe/C ratio is different than in Kiel. The Accelerator, which is used in Gif-sur-Yvette is

**Table 4.** Relationship between rapidity of CO<sub>2</sub> reduction on Fe powder and temperature (Stenström, 1994).

Temperature [°C]	Reaction rapidity [mb/min]
515	1.4
560	2.6
600	3.0
610	3.2
665	2.2
750	0.87



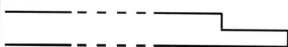
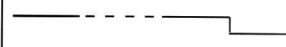
**Fig. 3.** Line for sealing and cracking quartz tubes, for cleaning CO<sub>2</sub> and measuring CO<sub>2</sub> amount. Part A is used for sealing the quartz tube, B – for cracking quartz tube and cleaning CO<sub>2</sub>, C – for measuring the amount of CO<sub>2</sub>, D – for collecting CO<sub>2</sub>.

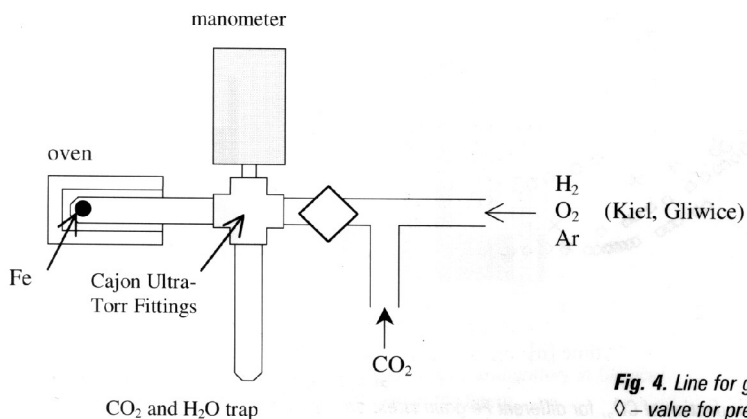
of older construction and to obtain adequate precision of dating,  $^{14}\text{C}$  concentration is measured for two graphite targets prepared from one sample. In the Kiel Laboratory, the  $^{14}\text{C}$  measurement is made for only one target.

After graphitisation, the sample is kept in atmosphere of argon (for maximum a few hours) and pressed into tablet of a few millimetres in diameter. So prepared target is ready to be placed in the accelerator.

Experience from the Laboratory in Kiel shows that the rate of reduction depends on the reactor size. If the tube diameter is bigger, the reaction is faster. In the German prototype the tube diameter of the reactor was 6 mm. Application of bigger diameter (9 mm) has shortened the reaction time to only 3 hours (**Table 5**). Oxidation and reduction of iron before introducing  $\text{CO}_2$  speed up the reaction, too.

**Table 5.** Comparison of procedures of  $\text{CO}_2$  reduction in several  $^{14}\text{C}$  laboratories. Reactor volumes are similar in all laboratories. The table presents current parameters, and those used in the prototype<sup>1)</sup> and in the test runs<sup>2)</sup>.

	Gif-sur-Yvette	Kiel	Gliwice
Reactor construction	Tube with Fe $\phi$ 6 mm, $\text{H}_2\text{O}$ trap welded	Tubes $\phi$ 9 mm ( $\phi$ 6 mm) <sup>1)</sup> , $\text{H}_2\text{O}$ trap connected with Cajon Ultra-Torr Fitting	Tube with Fe $\phi$ 6 mm, $\text{H}_2\text{O}$ trap ( $\phi$ 12 mm) connected with Cajon Ultra-Torr Fitting
Fe granulation	150 $\mu\text{m}$ , 44 $\mu\text{m}$	44 $\mu\text{m}$	(150 $\mu\text{m}$ , 10 $\mu\text{m}$ ) <sup>2)</sup> 44 $\mu\text{m}$
Fe amount	Measured individually for each sample	2 mg	(5 mg) <sup>2)</sup> 2 mg
Fe/C	5/1	2/1	(5/1) <sup>2)</sup> 2/1
Fe measurement	Weighing with accuracy 0.1 mg	Measurement with pipette	Weighing with accuracy 0.1 mg
Fe introduction to the quartz tube	Stainless tube 	Micropipette	Stainless tube 
Arrangement of Fe in tube	Grains situated closely to each other	Grains situated closely to each other	Grains situated closely to each other
$\text{CO}_2$ pressure	Dependent on the sample size	150-200 mbar	220-240 mbar
1 mg C	250 mbar	200 mbar	(230 mbar) <sup>2)</sup> 170 mbar
Reactor cleaning before the reduction	Heating the quartz tube with Fe in 650 $^\circ\text{C}$ and the reactor in 100 $^\circ\text{C}$ during 5 h under vacuum	Pumping the reactor with Fe overnight	Pumping the reactor with Fe overnight Heating the quartz tube with Fe in 650 $^\circ\text{C}$ and reactor in 100 $^\circ\text{C}$ during 5 h under vacuum and pumping the reactor overnight
Fe oxidation	None	700 mbar $\text{O}_2$ , $T=400$ $^\circ\text{C}$ , $t=15$ min	700 mbar $\text{O}_2$ , $T=400$ $^\circ\text{C}$ , $t=15$ min
Fe reduction	1000 mbar $\text{H}_2$ , $T=300$ $^\circ\text{C}$ , $t=1$ h	700 mbar $\text{H}_2$ , $T=400$ $^\circ\text{C}$ , $t=30$ min	700 mbar $\text{H}_2$ , $T=400$ $^\circ\text{C}$ , $t=30$ min
$\text{CO}_2$ reduction	250 mbar $\text{CO}_2$ /1 mg C, reduction time 5-7 h, reduction temp. 650 $^\circ\text{C}$	200 mbar $\text{CO}_2$ /1 mg C, reduction time 3 h, reduction temp. 600 $^\circ\text{C}$	170 mbar $\text{CO}_2$ /1 mg C, reduction time 4-5 h, reduction temp. 600 $^\circ\text{C}$
	Defreezing and pumping out the $\text{H}_2\text{O}_{\text{gas}}$ , Fe-C powder kept in reduction temp.	$\text{H}_2\text{O}$ frozen, Fe-C powder kept in room temp.	$\text{H}_2\text{O}_{\text{gas}}$ frozen, Fe-C powder kept in room temp.
	Introducing Ar before disconnecting the tube with Fe-C powder	Introducing Ar before disconnecting the tube with Fe-C powder	Introducing Ar before disconnecting the tube with Fe-C powder



**Fig. 4.** Line for graphitisation of  $\text{CO}_2$  (Gif-sur-Yvette and Kiel).  $\diamond$  - valve for precise measurement of gas amount.

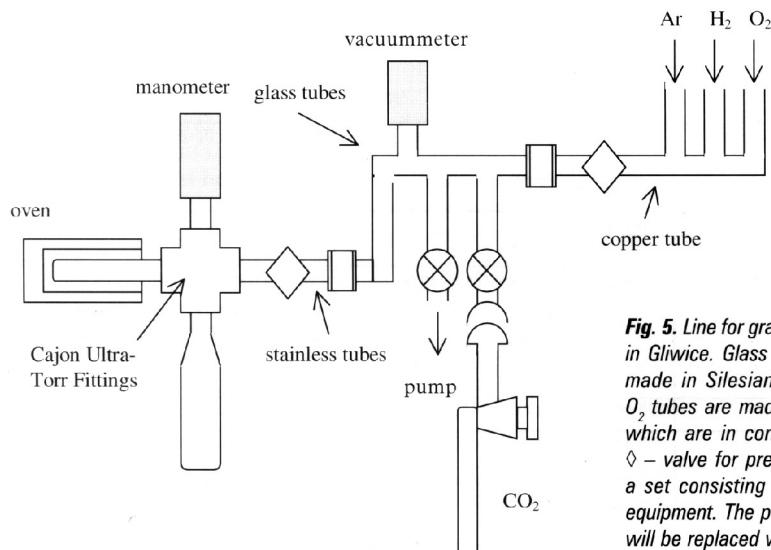
Construction of the Polish reactor (Fig. 5) resembles the scheme from French laboratory and the prototype from German Laboratory. That is why the tube diameter with Fe is small. Although tube diameters in Gliwice and Gif-sur-Yvette are the same, the time of reaction in Gliwice is shorter (Table 5) thanks to the oxidation of iron. In France, oxidation of iron is not used.

Primarily, in the reduction iron granulation coarser than now has been used (150  $\mu\text{m}$ ). After consulting members of the staff in the Kiel Laboratory, finer Fe granulation (ca. 44  $\mu\text{m}$ ) was applied. Sample is then more homogeneous. Originally the Fe/C ratio was 5/1, but because graphite targets will be sent to the Kiel Laboratory, the Fe/C ratio is adapted to the standards of that laboratory. For Fe introduction to the quartz tube, advantages of the French method with partly cut off one of ends of stainless tube has been taken (see figure in Table 5).

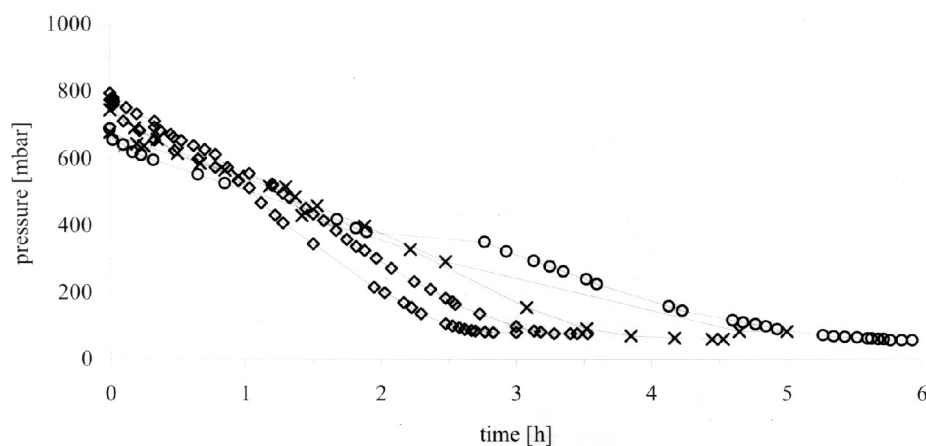
Before reduction the reactor is cleaned. In Gliwice two different ways of cleaning were in use: pumping cool reactor with Fe overnight, or heating the quartz tube with Fe in 650°C and the Cajon Ultra-Torr Fitting in 100°C during 5 h, and pumping overnight. At present the quartz tube with Fe is pumped and heated in 90°C overnight. Reduction parameters are similar to that in Kiel (the same temperature, 600°C, and amount of hydrogen, an excess 20%). The reduction time for such conditions and for Fe granulation 44  $\mu\text{m}$  is ca. 4 h (shorter than in Gif-sur-Yvette, longer than in Kiel).

## 6. TESTS OF GRAPHITISATION LINE

Tests were made for small portions of  $\text{CO}_2$  obtained from several samples in the Radiocarbon Laboratory in Gliwice. The  $\text{CO}_2$  amount corresponds to 1 mg carbon. First trials were made with Fe granulation 150  $\mu\text{m}$ . A few trials were also made for Fe granulation 10  $\mu\text{m}$ , but



**Fig. 5.** Line for graphitisation of  $\text{CO}_2$  in the Radiocarbon Laboratory in Gliwice. Glass elements and copper/stainless steel joints are made in Silesian Technical University workshops. Ar,  $\text{H}_2$  and  $\text{O}_2$  tubes are made of copper. Valves and other metal elements, which are in contact with  $\text{CO}_2$ , are made from stainless steel.  $\diamond$  – valve for precise measurement of gas amount. At present, a set consisting of rotary and diffusion pump works with the equipment. The pressure reaches  $10^{-4}$  hPa. In near future this set will be replaced with a turbomolecular pump.



**Fig. 6.** Changes of pressure in the reactor during reduction of  $\text{CO}_2$ , for different Fe grain sizes:  $\diamond$  – Fe 44 $\mu\text{m}$ , x – Fe 150 $\mu\text{m}$ , o – Fe 10 $\mu\text{m}$ .

the time of reduction was much longer than usually. Also the Fe weighing and introducing into the quartz tube was difficult for this granulation.

After consulting members of the staff in the Kiel Laboratory iron granulation 44  $\mu\text{m}$  was applied. Fig. 6 shows changes of pressure in the reactor for different Fe granulations. It is clear that the time of reduction is the shortest for Fe granulation 44  $\mu\text{m}$ .

Fig. 7 shows changes of pressure for different initial conditions. Different are the prerduction parameters

and the way in which the reactor was cleaned. It is visible that no significant differences in the rate of reduction occur. Probably the reaction is slightly slower when oxidation of Fe was made one day before reduction of  $\text{CO}_2$ , but this difference is not too distinct.

### 7. PRESSING THE Fe-C POWDER

When the graphitisation is completed the Fe-C powder is pressed into a tablet in aluminium holder adapted to install it in the ion source of accelerator. In Fig. 8 a device is shown for pressing the Fe-C powder. Ready graphite targets are stored in atmosphere of argon and will be sent to measurement in accelerator in Kiel.

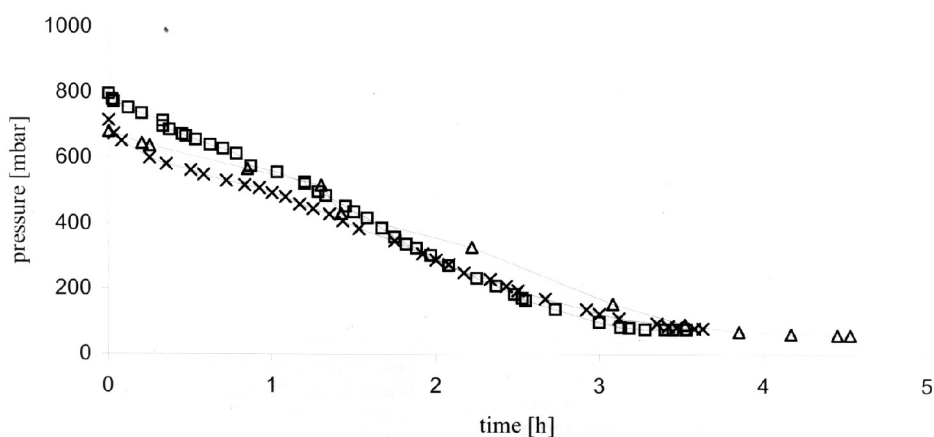


Fig. 7. Changes of pressure in the reactor during reduction of  $\text{CO}_2$  for different initial conditions:  $\diamond$  – cleaning the reactor for 24 hours, preoxidation and prerduction of the Fe;  $\times$  – heating of the quartz tube ( $650^\circ\text{C}$ ) and the union ( $90^\circ\text{C}$ ) for 1,5 hours, pumping out for 24 hours (room temperature), heating of the quartz tube ( $90^\circ\text{C}$ ), preoxidation and prerduction of Fe;  $\Delta$  – preoxidation and prerduction of the Fe, reduction of the  $\text{CO}_2$  in the next day.

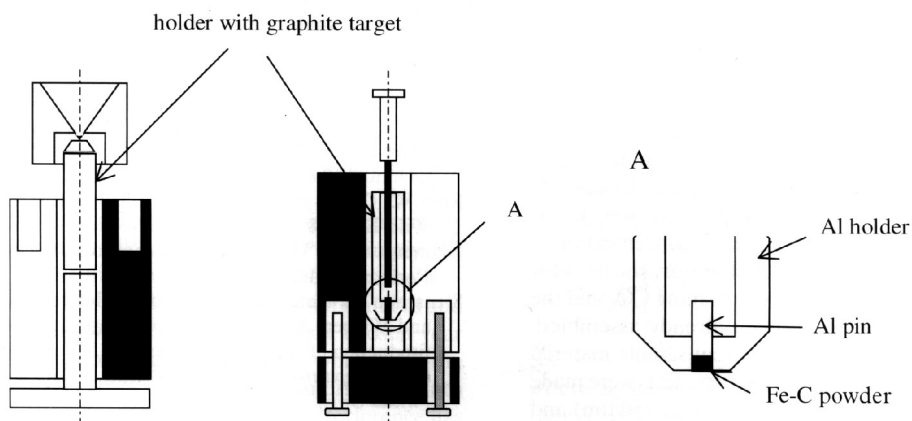


Fig. 8. Scheme of the press for making graphite targets (Laboratory in Gliwice). The details of part A are shown at the right side of the figure.

## 8. SUMMARY

The Accelerator Mass Spectrometry (AMS) is one of the techniques used in  $^{14}\text{C}$  dating. The advantage of this method is a small mass of the sample (a few mg).  $^{14}\text{C}$  concentration is measured in graphite, which is prepared from gaseous  $\text{CO}_2$  obtained from sample combustion. Graphite powder is pressed into target (a few millimetres in diameter), and then placed in the ion source of accelerator. In the source  $^{12}\text{C}^-$ ,  $^{13}\text{C}^-$  and  $^{14}\text{C}^-$  ions are sputtered from the graphite target by Cs beam.

In Europe, the accelerators are used in several laboratories. Graphite targets are produced in more laboratories. In the Gliwice Radiocarbon Laboratory a line to produce graphite targets is under construction. It contains equipment for sample preparation, sample combustion,  $\text{CO}_2$  purification and for production of graphite powder and graphite target.

The AAA method (Acid-Alkali-Acid) will be used for sample preparation. Samples will be treated with 0.5 M HCl in temperature  $50^\circ\text{C}$ . NaOH will be then used in room temperature. After each stage the samples will be rinsed with distilled water and the solution will be removed with glass micropipette until pH=7 is achieved. Dry samples will be placed in quartz tube together with copper oxide (0.5 g CuO per sample) and silver wool (0.15 g Ag per sample), pumped out and sealed under vacuum. Before this step CuO and Ag are preheated in a stream of oxygen. CuO is the source of oxygen needed for combustion, and Ag removes gaseous contamination of  $\text{CO}_2$ . Samples are combusted in muffle oven in temperature  $900^\circ\text{C}$  for a few hours. After combustion quartz tubes are cracked under vacuum, and the released  $\text{CO}_2$  is purified. Next the  $\text{CO}_2$  quantity corresponding to 1 mg C is separated for further processing.

Graphite powder arises during reduction of  $\text{CO}_2$  by  $\text{H}_2$  in high temperature. Fe powder is the catalyst of this reaction. In the reactor the necessary amount of  $\text{CO}_2$  is collected and  $\text{H}_2$  is introduced in an excess of 20%. The reaction yields water vapour and graphite powder, which is deposited on Fe grains. In order to maintain the reaction the  $\text{H}_2\text{O}_{\text{gas}}$  is continuously removed by freezing. The best temperature for this reaction is  $600^\circ\text{C}$ .

When the graphitisation is completed, Fe-C powder is kept in argon until it is pressed into graphite target. Such target is ready for AMS measurement. Ready graphite targets are kept in argon and will be sent to  $^{14}\text{C}$  Laboratory in Kiel to measure the  $^{14}\text{C}$  concentration.

In the Gliwice Radiocarbon Laboratory the lines for sealing and cracking quartz tubes, cleaning  $\text{CO}_2$  and the line for graphitisation have been already assembled. The last one was tested using different sample material obtained in conventional  $^{14}\text{C}$  laboratory. Tests were made for different Fe grain size (10  $\mu\text{m}$ , 44  $\mu\text{m}$ , 150  $\mu\text{m}$ ) and for different conditions at the beginning of the graphitisation. It seems that the best reduction occurs on Fe 44  $\mu\text{m}$ , and with the preoxidation and prereluction of Fe powder directly before the reduction of  $\text{CO}_2$ .

## ACKNOWLEDGEMENTS

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