^{14}C-SAMPLE PREPARATION FOR AMS MEASUREMENT

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Most of the sample preparation done so far was devoted to ^{14}C measurements. Therefore, currently used methods to prepare carbon samples suitable for use in the sputter ion source of VERA are described.

Basically, three steps are necessary to prepare ^{14}C samples for accelerator mass spectrometry:

a. adequate pretreatment of the sample material;

b. complete combustion of the carbon contained in the sample to CO_2;

c. conversion of CO_2 to elemental carbon as target material.

a. Pretreatment procedures

The aim of the pretreatment procedures is the removal of non-indigenous carbon from the sample by physical and chemical means. In most cases the samples are first cleaned in an ultrasonic bath to remove adherent particles. As a further pretreatment for sample materials such as charcoal, textiles, peat, etc., the so-called ABA (acid-base-acid, sometimes also referred to as AAA acid-alkaline-acid) method is applied. The samples are first soaked in diluted hydrochloric acid to dissolve any carbonates possibly present in the sample due to ground water percolation. Afterwards humic acids are removed with diluted sodium hydroxide solution. A final acid wash ensures that CO_2 which may have been absorbed during the alkaline step is removed from the sample. The temperature at which the samples are held during the individual steps, as well as the duration of the treatment and the degree of dilution of the acid and the base, are varied according to the nature of the particular sample to prevent the dissolution of too much sample material. Between each step, and at the end of the procedure, the samples are washed to almost neutral with double-distilled water.

For radiocarbon dating of fossil bones only the organic fraction of the bone can be used since carbonates of the inorganic bone matrix may exchange with the environment during burial times. The cleaned bone sample is ground and the inorganic component of the bone is dissolved in hydrochloric acid. Humic acids are soluble in sodium hydroxide whereas bone collagen is only slightly soluble in this agent. Therefore the organic residue of the bone is treated with diluted sodium hydroxide in the next cleaning step. An additional clean up of the bone sample is achieved by the gelatinisation of the collagen. The residue of the alkaline step is washed to neutral and dissolved in acidified (pH $\approx$ 3) double-distilled water at a temperature of 90°C. The solution is centrifuged and evaporated to dryness, which yields the gelatine fraction. Further cleaning will be necessary for critical bone samples which either may only contain highly degraded collagen or which are suspected to be contaminated with non-indigenous carbon. Very

elaborate procedures for the isolation of indigenous carbon compounds from such critical bone samples have been developed by various laboratories. These methods are not used as routine methods for the pretreatment of bone samples because they are very time consuming and additional pretreatment steps increase the danger of contamination.

b. Combustion of the samples

An amount of 10 mg of the cleaned and dried sample material is transferred to a quartz tube which contains 1 g CuO. Some silver wire is added as a binder for sulfur and halogens and the tubes are evacuated and sealed with a glass blower torch. For complete combustion the sealed samples are heated for ~~two~~ hours in a muffle furnace at 900°C.

Before use the quartz tubes are preheated for one hour at 950°C, the CuO for two hours at 900°C. The silver wire is washed with 1M HCl, double-distilled water and acetone (*p.a.*) and heated at 550°C for one hour.

c. Conversion of CO_2 to elemental carbon

Solid carbon target material is needed for the measurement of the $^{14}C/^{12}C$ ratios with the accelerator mass spectrometer. Therefore the CO_2 produced during the sample combustion must be transformed to elemental carbon. The catalytic reduction of CO_2 with H_2 to carbon over Fe or Co according to the reaction

$$CO_2 + 2H_2 \xrightarrow[580°C]{Fe} C + 2H_2O$$

has been adapted from Vogel *et al.* [1]. This "graphitisation" technique is now a standard method used by many AMS ^{14}C laboratories and was also chosen for the VERA lab.

Fig. 1 shows a schematic display of the graphitisation apparatus. The whole gas transfer and vacuum line is made from stainless steel high purity gas handling components. The three reactors are each built from a quartz and a Duran glass vial fixed to a stainless steel cross via Ultra Torr fittings. The cross is equipped with suitable adapters for their connection to the gas handling line and the mounting of a piezo-resistive pressure transducer to monitor the pressure in the reaction vessels. The volume of the reactors was determined as ~19.5 cm^3, ~18.7 cm^3 and ~12 cm^3. A turbomolecular drag pump together with a diaphragm roughing pump is used to achieve an oilfree vacuum to avoid contamination of the samples during the graphitisation. A water reservoir is mounted to one end of the system because the transfer line is filled for cleaning with ~ 20 mbar water vapor whenever it is not in use. The other end of the line comprises the H_2 inlet to the system.

Before the graphitisation is started, ~~Co~~ Fe powder is weighed into the quartz tubes of the reactors and cleaned at 300°C for 45 minutes in vacuum. After cooling to room temperature, about 800 mbar H_2 is added and the catalyst is treated again at 300°C for

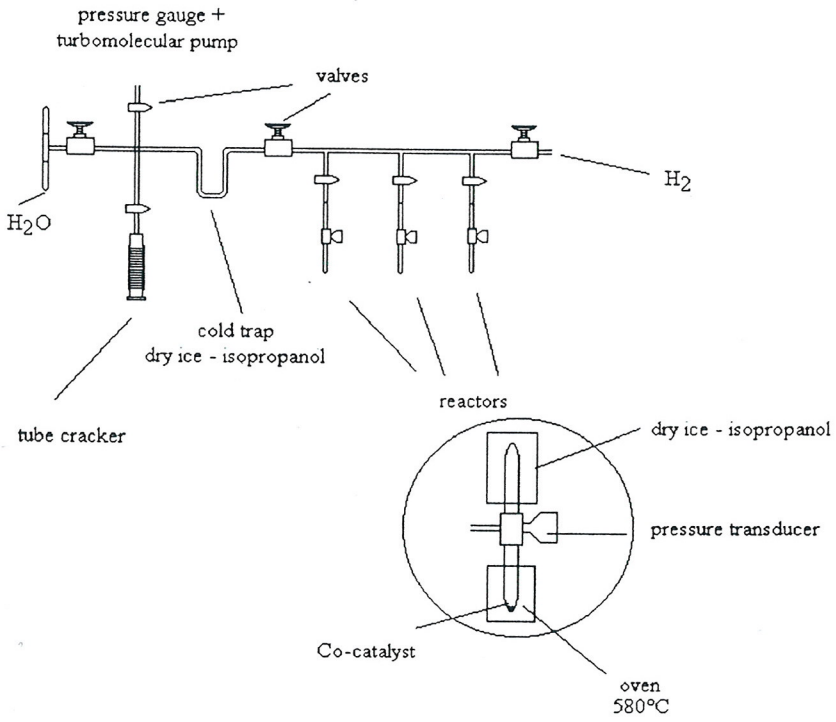

Fig. 1: Schematic view of the graphitisation system.

another 45 minutes. This procedure removes traces of CO_2 from the catalyst by degassing and formation of CH_4. The amount of Co catalyst used corresponds to a mass ratio Co:C ≈ 3 if the reactors are filled with 300 mbar CO_2.

The combustion tube is transferred into the tube cracker of the apparatus and the system is evacuated to a pressure < 10^{-4} mbar. The tube is cracked, H_2O is frozen out in a cold trap with a ~~mixture of dry ice and~~ isopropanol (-78°C) and the CO_2 is cryogenically transferred to the reaction vessels with liquid nitrogen. Non-condensable gases are evacuated and the reactor valve is closed. The CO_2 is brought to room temperature and the amount of CO_2 gas which has been produced during the combustion is measured with the pressure transducer. For sample materials with a known carbon content this gives a check whether the combustion of the sample is quantitative. The CO_2 pressure in the reactor is adjusted to about 300 mbar by expanding the gas to various volumes of the transfer line. A stoicheometric amount plus an excess of 100 mbar H_2 (e.g. 700 mbar H_2 for 300 mbar CO_2) is added to the CO_2, leading to a total pressure of about 1 bar at the start of the graphitisation process. If less than 300 mbar CO_2 is collected, even in the volume of the smaller reactor, the graphitisation is performed at lower pressure. The catalyst in the quartz tube is heated to 580°C and the H_2O produced during the chemical reaction is removed from the gas by cooling the Duran glass tube with a ~~dry-ice~~ isopropanol bath (see Fig. 1). During the entire graphitisation process the pressure is monitored. The reaction is complete after 6 to 7 hours when all the CO_2 is reduced to elemental carbon (Fig. 2), which is deposited on the Co catalyst and only the excess of

H_2 is present in the gas volume. The carbon together with the catalyst is used as target material for the ^{14}C-measurements. The Fe-C mixture is pressed into the 1-mm holes of the aluminum target holders with a recess of 0.5 mm. Up to 40 targets can be loaded into the sputter ion source of VERA. These targets produce $^{12}C^-$ currents in the range of 15 to 20 μA at relatively "cold" running conditions of the ion source.

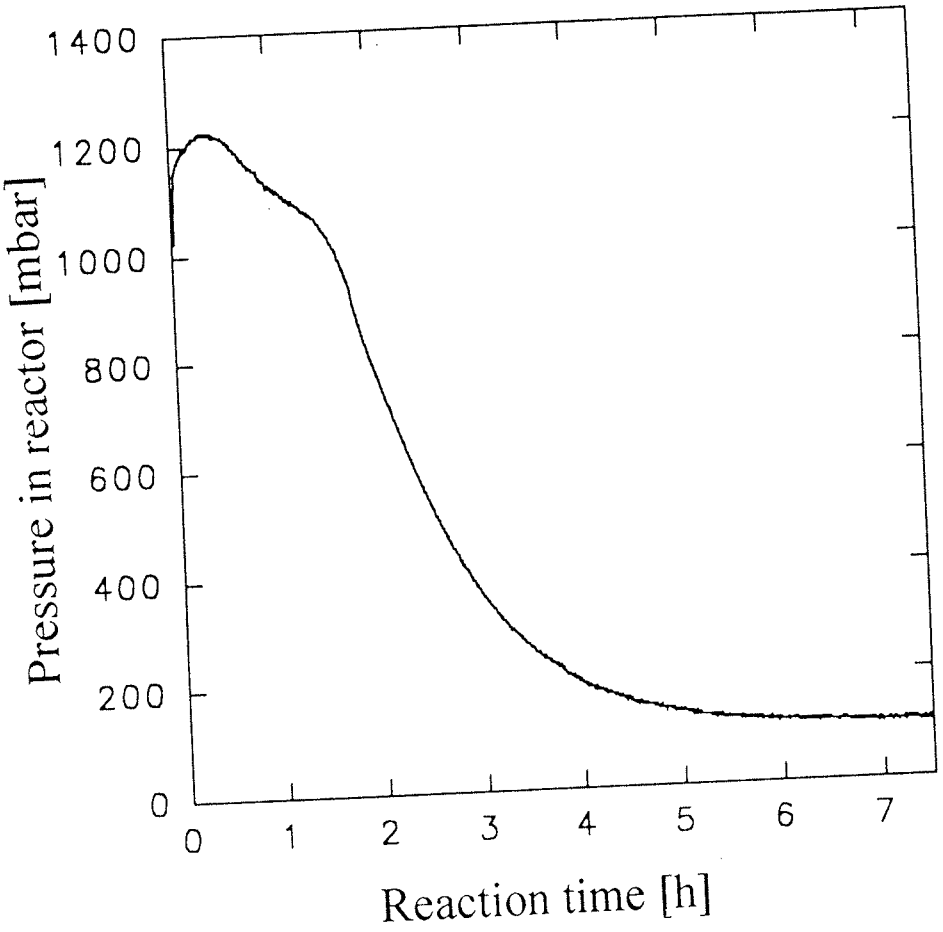

Fig. 2: Variation of the total pressure (initially CO_2 plus H_2) in the reactor during graphitisation.

With the method described above several targets for the accelerator mass spectrometer have been produced. In the first stage of the target production the CuO has not been pretreated and the first chemistry background measurement yielded a background of ~1.5 pMC (i.e., percent modern carbon). A reduction of the background to less than 0.5 pMC has been achieved by the pretreatment of the CuO.

The number of targets produced for the accelerator performance, reduction of the chemistry background and first age determinations from different materials (standards, chemistry blanks and samples) up to now are given in Table 1.

Sample material	Number of targets
Oxalic acid II	5
C3-Cellulose	32
C5-Wood	5
C6-Sucrose	34
Bone	33
Soft tissue	35
Chemistry blanks	65
Catalyst blanks	2
Total	211

Table 1: Number of targets produced from different materials.

[1] J.S. Vogel, J.R. Southon, D.E. Nelson and T.A. Brown, Nucl. Instr. Meth. B **5**, 289 (1984).

RESULTS OF SYSTEMATIC MEASUREMENTS WITH ^{14}C AND FIRST RESULTS OF RADIOCARBON DATING WITH VERA

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A new AMS facility such as VERA requires extensive measurements with ^{14}C samples of known content (standards) in order to establish the highest level of precision attainable. The first results summarized in Fig. 1 were presented at the 7th International AMS Conference in Tucson, Arizona, in May 1996 [1]. Systematic tests were continued throughout the year 1996, helping us to gain confidence in the overall reproducibility of ^{14}C measurements and in the precision of actual radiocarbon dating experiments.

One of the basic sources of uncertainty is the fact that unknown samples and standard samples are individually prepared samples located in different positions of the sample wheel. Besides other possible differences, there may be a position dependence of the measured $^{14}C/^{12}C$ ratios. The relatively high precision achieved for the standard materials shown in Fig. 1 stems from using several samples of the same material in different wheel positions and forming a mean value. However, this is time consuming, and in addition requires more sample material than a single-sample measurement. In order to make reliable measurements from single samples, we are currently studying this effect in great detail. Contrary to first indications of a position dependence, we now feel that the highest precision achievable depends primarily on the quality of the tuning of