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Kunio OMOTO

1 Preface

The Institute of Geography, Faculty of Science of Tohoku University has carried out more than 1,200 radiocarbon determinations up to the end of July 1985. The number will be ranked third among ten radiocarbon dating laboratories in Japan. The results have been reported by Nishimura *et al.* (1972), Omoto *et al.* (1974), Omoto (1976), Omoto *et al.* (1976), Omoto (1977, 1978 and 1979), and by the Radiocabon Dating Committee of Tohoku University (1982 and 1984).

In these five years, several changes with respect to financial support, administration and the dating systems have been accomplished. In this paper, the author aims to describe two remarkable progress marked by himself and recent radiocarbon dating systems of the Institute of Geography, Faculty of Science of Tohoku University.

The first progress was a development of "Full Automatic Radiocarbon Dating System" linked to a personal computer system (Omoto 1982), and since then gas proportional counting has been extremely stable, resulting in the production of accurate dates with small uncertainties.

The second was the extension of the detectable T-max age of old samples up to 65,000 y BP without using any enrichment techniques such as those developed by Grootes *et al.* (1975), but by using a low-background liquid scintillation spectrometer linked to a personal computer system (Omoto 1983).

Together with these new developments, present sample processing techniques will be described which enable much more reliable radiocarbon determinations to be carried out.

2 Development of automatic radiocarbon dating

In radiocabon dating, especially in gas proportional counting system, decays of β-rays are quite random phenomena, so that it is necessary to continue counting for at least 1,000 minutes in order to obtain significant statistical data. It is sometimes difficult to keep ideal counting parameters over the total counting time.

Many radiocarbon dating laboratories therefore often fix their counting conditions

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i.e. pressure of the sample gas and temperature of the counter, *etc.* If these conditions were kept strictly, the high voltage setting for the counter should be fixed. It may be possible for this to be done in some laboratories where routine dating has been carried out for a long time, because they would have skilled operators who could optimise counting conditions.

Even if optimal conditions are maintained, errors occurring because of wrong equipment settings and drifts of temperature and high voltage for the center counter have often been significant. Strictly speaking, if we need more accurate and reliable dates, we must maintain our instruments in optimal condition during total counting time.

In our Institute of Geography, staff members including graduate students run their own samples, although they are not always skilled operators. Therefore it was necessary for the author to introduce a personal computer system linked to radiocarbon dating instruments, in order to control instrument parameters, control the high voltage so that it remains constant throughout the counting period, and carry out data processing, saving much time. Two systems have been developed for gas proportional

Tabl 1 Radiocarbon dating programs for gas proportional counting.

File name	Purpose of use	Size of disk	Computer
AGE	Age calculation	5'	PC−8001
AGE−88	*do.*	8'	PC−8801
ARCD	Start of experiment (job select)	5'	PC−8001
ARCD−88	*do.*	8'	PC−8801
ESG	Exchange of sample gas	5'	PC−8001
ESG−88	*do.*	8'	PC−8801
GCP	Guard counter plateau measurement	5'	PC−8001
GCP−88	*do.*	8'	PC−8801
HV OFF	High voltage turn off	5'	PC−8001
HV OFF	*do.*	8'	PC−8801
HV−ON	High voltage turn on	5'	PC−8001
HV−ON	*do.*	8'	PC−8801
LPT	Experiment under low pressure	5'	PC−8001
LPT−88	*do.*	8'	PC−8801
MTN	Data file maintenance	5'	PC−8001
MTN−88	*do.*	8'	PC−8801
NBS	Calculation of NBS value	5'	PC−8001
NBS−88	*do.*	8'	PC−8801
RCD	Automatic plateau and β-rays measurement	5'	PC−8001
RCD−88	*do.*	8'	PC−8801

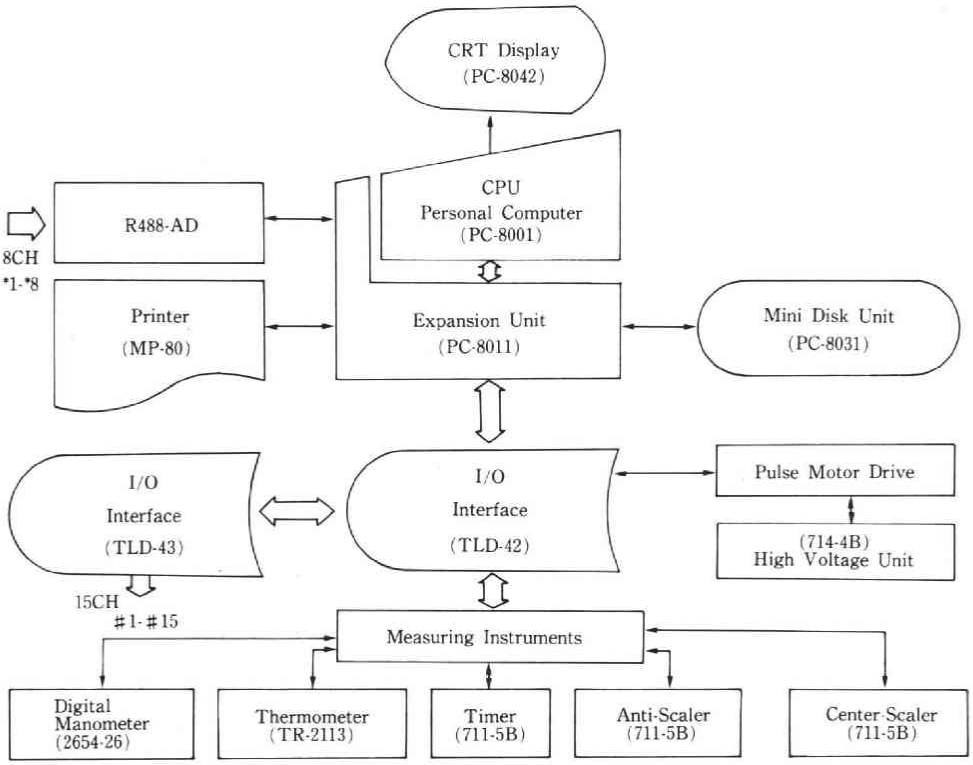


Fig. 1 A diagram indicating a personal computer system linked to No. 1 gas proportional counting equipment (modified after Omoto 1982).

counting. One is a "fully automatic radiocarbon dating system" whose characteristics have been reported (Omoto 1982), and another is "automatic radiocarbon dating system". When we use former system, we only need to arrange a new metal reservoir filled with sample gas before counting. In the latter case, we must change reservoir flask filled with sample gas every time before counting by manual mode. The computer executes "plateau measurement program" after initialization, then it determines "optimal high voltage value" for the center counter. The high voltage value is set automatically based on the commands from CPU. Then the computer executes "automatic β-rays counting program". These processes are controlled by software programs written by the author. Algorisms, details of experiments, and lists of software programs have been explained in a previous report (Omoto 1982). Table 1 indicates file names for gas proportional counting.

Fig. 1, 2 and 3 indicate present computer systems linked to the radiocarbon dating equipments. In addition, a fully automatic PC-9801 series computer system is connected to a 300 ml gas proportional counter. The software programs are essentially

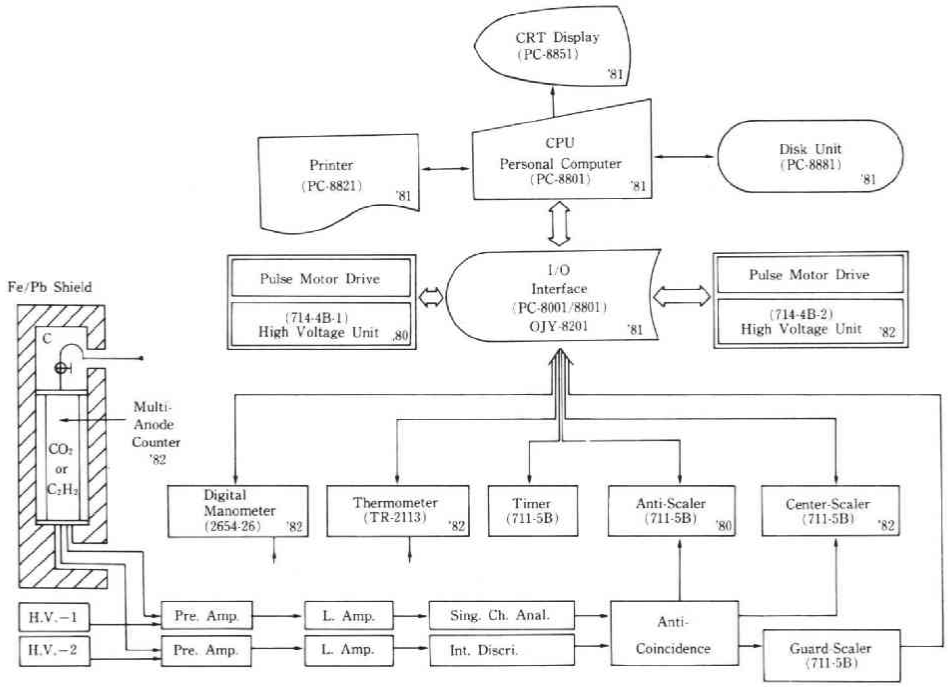


Fig. 2 A diagram indicating a personal computer system linked to No. 2 gas proportional counting equipment.

based on the BASIC programs reported previously (Omoto 1982 and 1983), but they have been rewritten more concisely for faster and more efficient program execution. These systems have eliminated most laboratory errors, and more reliable dates with much smaller errors have been obtained.

3 Extension of detectable age range

Many laboratories and industries have sought superior equipment for radiocarbon dating in order to detect lower-radioactivity and to determine ages >40,000 y BP with smaller errors (<1,000 y). The equipment used must combine a very low background with high counting efficiency.

In order to reduce background, special underground chambers lined with 40 cm of special concrete and overlain by 70 m water equivalent sandstone have been constructed (Stuiver *et al.* 1979, Ulrich *et al.* 1980, Loosli *et al.* 1980, Oeschger *et al.* 1981).

In the 1970's, development of liquid scintillation spectrometers in the pharmacy and radioisotope chemistry made it possible to measure the activity of a relatively large quantity of carbon in a small liquid volume. Since the late 1970's the development of bialkali photomultiplier tubes with high sensitivity and low noise, whose

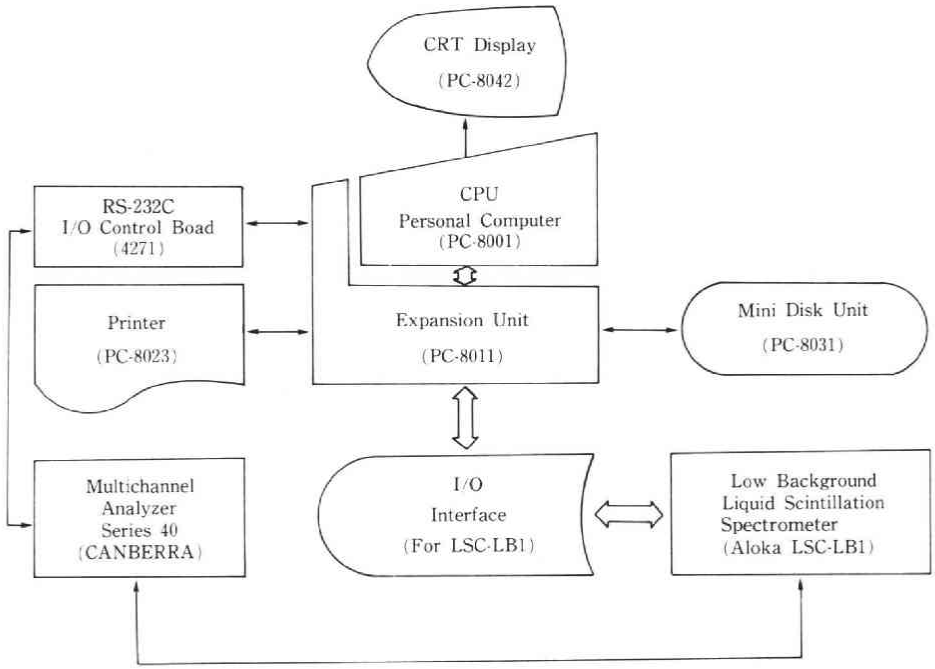


Fig. 3 A diagram indicating a personal computer system linked to a liquid scintillation spectrometer (modified after Omoto 1983).

spectral response matches many organic cocktails, has allowed the liquid scintillation spectrometer to be successfully applied for radiocarbon dating, using pulse height discriminator, anti-coincidence circuit. The performance of these systems can be superior to gas proportional counting systems.

Fortunately, the author could purchase a low-background liquid scintillation spectrometer (Aloka LBS-1) in 1981, based on financial support from the Ministry of Education as a Grant in Aid for Scientific Research (Chief investigator K. Omoto: Nos. 542061 and 00542061). It indicated high capability which was proved by its low background with high counting efficiency (Omoto 1983) by using a 20 ml Teflon vial. Therefore if we can produce a large quantity of benzene by repeated chemical assays, we are able to extend T-max age (the oldest limit of detectable age) of samples to greater than 60,000 y BP with 3 days counting.

Theoretically speaking, the T-max age produced from the system may reach 65,000 y BP, however many samples whose true ages are within 65,000~70,000 years will provide younger ages because of the incorporation of a small amount of younger carbon-containing material.

Incorporation of as little as 0.5% of modern carbon can make a vast difference in

Table 2 Radiocarbon dating programs for liquid scintillation spectrometry.

File name	Purpose of use	Size of disk	Computer
AGE	Age calculation	5'	PC−8001
CAL	Calibration of efficiency curve	*do.*	*do.*
EFF	Calculation of efficiency	*do.*	*do.*
EX-1*	Print out start channel and band width of ROI for MCA-4271	*do.*	*do.*
EX-2*	Setting number of ROI for MCA-4271	*do.*	*do.*
EX-3*	Read and write MCA-4271 data	*do.*	*do.*
EX-4*	Transfer EX-3 data to MCA-4271	*do.*	*do.*
EX-5*	Print out ROI data of MCA-4271	*do.*	*do.*
H-3	Tritium counting	*do.*	*do.*
L-MTN	Data file maintenance	*do.*	*do.*
LSC	Liquid scintillation spectrometry	*do.*	*do.*
MCA.BAS*	Control of MCA-4271	*do.*	*do.*

*Developed by Toyo Corporation and modified by the author.

C-14 age within this range (Omoto 1983). Because of this, pretreatment techniques for the removal of younger contamination are badly needed.

It was found that the background value for an 8 ml vial was significantly lower than that for a 20 ml vial, using a volume of synthesised benzene between 3.5 and 5.0 ml for each assay (Omoto 1983). If we expect optimum condition, we can recommend the use of an 8 ml vial. Previously, there were no standard samples for 8 ml vial, so the counting efficiency of these vials were determined by using 20 ml standard samples. In 1983, when 8 ml standard samples were available, ages for unknown samples were determined, providing much better results than expected. These facts suggest that routine counting is possible using vials having a volume of 8 ml or smaller. The chemical assays using less material may save much time for an operator.

The system is also connected with personal computer system (NEC PC-8001 series) and multi-channel spectrometer (Canberra's MCA-4271), as shown in Fig. 3. The software programs for them have been developed by the author (Omoto 1983), and their file names together with their purpose of the use are shown in Table 2.

4 Sample processing

In our Institute of Geography, staff members and students of the geomorphology course have collected their samples in their field surveys and have processed their own samples. The author believes this is a very good system because staff and students obtain much more useful first-hand information than they would obtain those from

other radiocarbon laboratories.

At present, many laboratories have applied A.A.A. (3A) system in processing organic materials, *i.e.* treated with diluted HCl in the first place, washed with distilled water, treated with dilute NaOH in the second place, washed again by distilled water, and finally acidified before being dried.

Wood samples are cut into slivers about 5 cm in length before chemical treatment. After treatment, the samples are placed in crucible, covered with quartz sand, and are then baked. The quartz sand is removed before combusion.

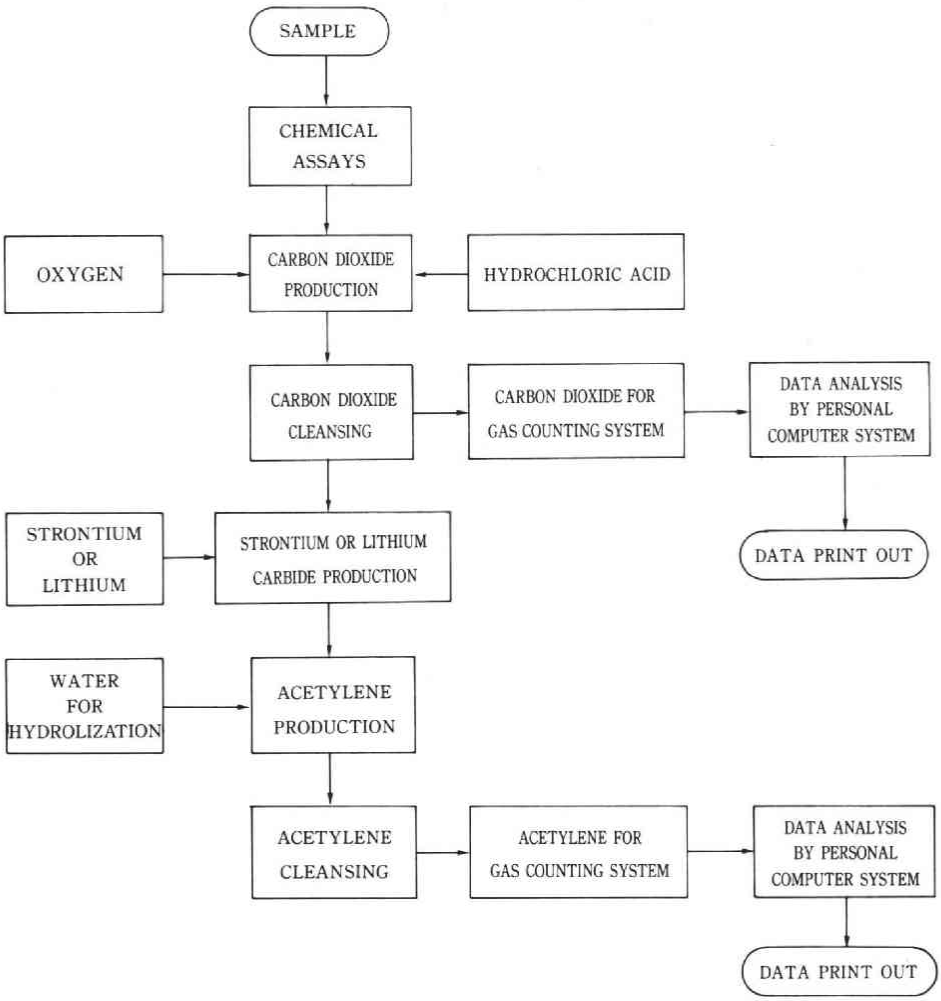
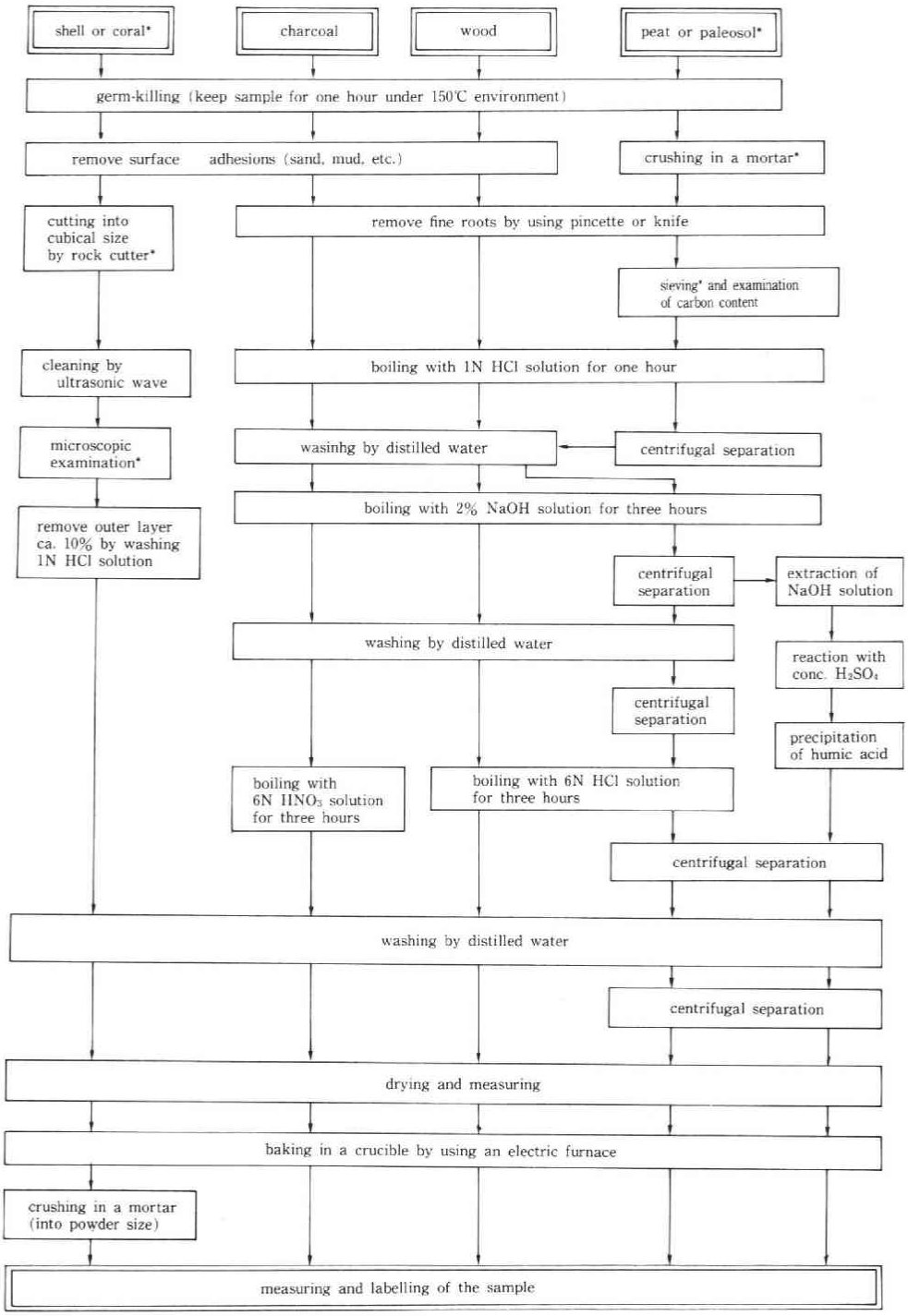


Fig. 4 A flow chart indicating a production of the sample gas for gas proportional counting (modified after Omoto 1983).


shell or coral*
charcoal
wood
peat or paleosol*
germ-killing (keep sample for one hour under 150℃ environment)
remove surface adhesions (sand, mud, etc.)
crushing in a mortar*
cutting into cubical size by rock cutter*
remove fine roots by using pincette or knife
sieving* and examination of carbon content
cleaning by ultrasonic wave
boiling with 1N HCl solution for one hour
microscopic examination*
wasinhg by distilled water
centrifugal separation
boiling with 2% NaOH solution for three hours
remove outer layer ca. 10% by washing 1N HCl solution
centrifugal separation
extraction of NaOH solution
washing by distilled water
reaction with conc. H_2SO_4
centrifugal separation
precipitation of humic acid
boiling with 6N HNO_3 solution for three hours
boiling with 6N HCl solution for three hours
centrifugal separation
washing by distilled water
centrifugal separation
drying and measuring
baking in a crucible by using an electric furnace
crushing in a mortar (into powder size)
measuring and labelling of the sample

Paleosols and peats are dried and crushed using a mortar and pestle. Most coarse grains and roots are removed by hand picking, and the sample is finally sieved to remove any coarse material remaining. These samples are then analysed for carbon content. Charcoal samples are examined for root materials, and these, together with adhering sand or soil, are removed physically. Charcoal, paleosols and peats are then given the A.A.A. treatment. After chemical treatment , each sample is placed in a crucible and is baked in an electric furnace. The baked samples are then placed in a quartz tube and are burned in a stream of oxygen (Omoto 1980a and 1980b). The carbon dioxide thus produced is bubbled into a flask containing dilute ammonia solution.

Shell and coral samples are pretreated as follows: The samples are washed with distilled water in an ultrasonic bath, and 10% of the surface is removed using dilute acid solution. Organic materials adhered on its surface are burned away in the electric furnace in the next stage. Then the sample is crushed in a mortar into fine powder size, which is treated with dilute acid again to produce carbon dioxide. The carbon dioxide is bubbled into a flask containing dilute ammonia water. This chemical treatment is used by most laboratories, and has been reported by the author (Omoto 1980a, 1980b and 1983).

This laboratory very rarely dates bone samples, which provide sometimes false dates for many archaeologists. There are many kinds of suggestions in treating bone sample, but the author considers that the EDTA method developed by El-Daoushy *et al.* (1978) must give us most reliable results at the moment.

Sometimes acetylene gas is used as a sample gas in the gas proportional counters. This is produced from strontium carbide or lithium carbide. The method of synthesis is shown chemically in Fig. 4. Treatments described above are summarised and shown schematically in Fig. 5.

5 Concluding remarks

The author described two recent progress made in these five years by himself. They were both accomplished by use of personal computer systems, linked to radiocarbon dating instruments. The results indicated improved dates with reduced uncertainties compared with the former one. Then he had a firm confidence that these systems might be one of the systems which had been sought for a long time by many laboratories in the world, and that their working condition and the accuracy might indicate a culmination and a limitation both in gas proportional counting system and liquid scintillation spectrometry. He also described recent pretreatment techniques of the sample materials.

Fig. 5 A diagram indicating sample processings in the radiocarbon dating experiment of the Tohoku University.

Accelerator mass spectrometry (AMS), a new radiocarbon dating technique, is now opening a new page in the history of radiocarbon dating. It promises us that it can yield a reliable date from very small amount of sample (in mg size), which is unable to be dated in the present routine gas proportional counting system and liquid scintillation spectrometry. Using such new dating techniques, rapid progress and development in geochronology and related sciences may be accelerated in near future.

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