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ENRICHMENT OF ^{14}C AND SAMPLE PREPARATION FOR BETA AND ION COUNTING

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ABSTRACT. We here report on two technical research projects of the Quaternary Isotope Laboratory (QL) *vis,* (1) the use of thermal diffusion isotopic enrichment to extend the technical range of ^{14}C dating, (2) the preparation of samples for ion counting using a Van de Graaff tandem accelerator. The second project is carried out in cooperation with, and partly at, the Nuclear Physics Laboratory.

A gain in dating range of 3 to 4 half-lives can routinely be obtained with the QL and the Groningen enrichment systems. The same gain in age range can be obtained for ion counting with a simplified system that requires only 0.5 to 2g of carbon and 3 to 7 days enrichment time.

A method to convert CO_2 quantitatively via CO into carbon is described. For short intervals the carbon deposit yields good $^{12}C^-$ beams. We also give a different procedure to make graphite-like carbon samples. The preparation of beryllium metal samples is given last.

Extending the range of ^{14}C dating

It is difficult to increase substantially the technical range of β-decay counting by reducing the background counting rate or increasing the recent counting rate of the counting setup, because much effort has already been expended on these points. Concentrating the ^{14}C in the sample by a known amount, however, can considerably extend the technical range of any counting setup. The increase can be of the order of 20,000 years for a practical system.

At present, three techniques have been proposed and used for ^{14}C enrichment (table 1). The laser enrichment technique is relatively new and, so far, has only been used in small-scale feasibility studies. Thermal diffusion enrichment in columns has been known for about 40 years (Clusius and Dickel, 1938) and has been connected to ^{14}C dating for over 30 years (Anderson and others, 1947). At the moment, only two systems, both using CO, are in routine operation, one at the Quaternary Isotope Laboratory (QL), Seattle, and one in Groningen (GrN). We limit our discussion to CO enrichment.

The construction of the thermal diffusion column and of the Groningen enrichment system was given by Grootes and others (1975). The QL system has been described by Grootes and Stuiver (1979).

The QL system consists of 23 single columns combined to 5 completely independent systems. Each has 3 or 4 columns in parallel in a top section connected in series with a single column. Each top column has its own reservoir ($\approx$5l). At GrN, 18 single columns are used. These are combined into 9 parallel groups of 2 columns in series with each other. In contrast to the QL system, the 9 top columns are connected to a com-

TABLE 1

^{14}C enrichment systems

Thermal diffusion	CO	Groningen*	Grootes and others, 1975; Grootes, 1977
	CO	Quaternary Isotope Lab (QL) Seattle*	Stuiver, Heusser, and I C Yang, 1978 Grootes and Stuiver, 1979
	CH_4	Kiel	Erlenkeuser, 1971a, b; 1976
	CH_4	Vienna	Pak, 1970; Felber and Pak, 1972
	CH_4	Munich	Kretner, 1973; Kretner and Dickel, 1975
Laser excitation	CH_2O	Oxford	Hedges and Moore, 1978

* System in routine operation for ^{14}C dating.

mon reservoir at the top. The enrichment conditions are about the same for the two systems.

Technical dating range

The technical age range for ^{14}C and other dating methods is determined by the ratio of the net counting rate for a recent sample and the minimum detectable net sample counting rate.

In β-decay counting with a proportional counter or liquid scintillation setup as well as in ion counting using an accelerator, a non-zero count rate is observed for a sample that presumably does not contain a measurable amount of ^{14}C (or ^{10}Be) (background). The minimum measurable amount of ^{14}C (or ^{10}Be) follows from the requirement that the difference between the observed gross sample counting rate and the background counting rate be more than twice the uncertainty in the background (2σ criterion). For a good proportional counter setup this uncertainty is determined mainly by counting statistics (Stuiver, 1978). For ion counting using accelerators, other factors, such as fluctuations in ion source emission and in accelerator transmission efficiency, add to the experimental uncertainty.

For the best proportional or liquid scintillation setups, the range of ^{14}C dating at present is 55,000 to 60,000 years. For electrostatic accelerators, a dating range from about 40,000 to 70,000 has been reported (Bennet and others, 1978). This range estimate was based on the apparent age of a graphite sample, calculated directly from its observed ^{14}C ion counting rate. As discussed above, this is not a true measure of the dating range. The true range may be considerably larger or smaller, depending on the stability and reproducibility of the machine conditions that can be obtained. Also the range may depend upon the success that can be achieved in eliminating ions not originating in the source material and in preventing cross-contamination among sources.

The use of CO has been found practical because it is prepared easily in large quantities by passing CO_2 through a hot zinc-asbestos mixture (10 to 1 by weight) at $\approx 400°C$. It has good thermal diffusion properties and offers the possibility of determining the ^{14}CO enrichment from an empirical ^{14}CO-mass 30 enrichment relation by measuring mass spectrometrically the simultaneous enrichment of the isobaric molecule $^{12}C^{18}O$.

A practical enrichment system should be fairly easy to build and its performance should not depend critically on the specific details of its construction. Grootes and Stuiver (1979) discussed the performance of the QL system in detail and compared it with theory and with that of the Groningen system. Both systems showed a reasonable reproducibility for the enrichment of different samples under the same conditions. The observed enrichment was only about half of the theoretical value for both systems. Varying the theoretical transport coefficients to obtain agreement with the experimental results showed that the effective thermal diffusion transport coefficient (H_{eff}) is close to its theoretical value but that the effective mixing coefficient (K_{eff}) is much larger (but similar) for both systems. These results suggest that the performance of a hot wire-column enrichment system is sufficiently insensitive to system geometry (1, 3, or 4 columns to 1) and precise column construction (spacers). Systems of the QL and GrN design (built fairly easily by a skilled glassblower) can therefore be expected to add 3 to 4 half-lives to the ^{14}C dating range of any laboratory using them. The most costly component of such systems is the Pt-Ir wire. The main disadvantage is their limited output (10 to 12 samples a year) and the large amount of sample needed.

The systems discussed above produce gram quantities of enriched carbon for large proportional β-decay counters. The development of direct counting of ^{14}C ions produced by an electrostatic accelerator has made it possible to measure the ^{14}C content of milligram quantities of carbon (Bennet and others, 1977; 1978; Muller, Stephenson, and Mast, 1978; Nelson, Korteling, and Stott, 1977). At the milligram level, laser enrichment of CH_2O as discussed by Hedges and Moore (1978) may become viable. For thermal diffusion enrichment of CO, the small quantities of enriched material required for ion counting make it possible to enrich in a simple and much smaller setup for a shorter time or to reach a much higher enrichment.

For an ideal enrichment system, the volume of the enrichment column is negligible, so the heavy isotope is distributed essentially between the enrichment volume at the bottom of the column and the reservoir at the top. Decreasing the column diameter and thereby minimizing the column volume, however, also decreases the net isotopic mass transport through the column and, thus, increases the time needed to obtain a certain enrichment. To obtain a milligram quantity of highly enriched gas from a total sample of about a gram, it is advantageous to extract only the gas at the bottom of the column and to use a small diameter column.

We have calculated the equilibrium separation factor $q_e{}^{14}C^{16}O$ ($\equiv$ the isotope ratio of the enriched isotopic molecule in the enrichment volume divided by the isotope ratio of the same in the reservoir, when the final enrichment equilibrium has been reached) as a function of pressure for columns of various column diameter r_1 and a constant ratio of column diameter to wire diameter ($r_1/r_2 = 30$) (fig 1). As shown, the separation factor increases strongly with decreasing column diameter. The pressure for which the maximum separation factor is obtained also increases as the column diameter decreases.

The quantity of interest in a practical enrichment system is the enrichment that can be obtained in a fixed amount of gas in a certain (preferably short) time. The ultimate enrichment is determined by the separation factor and by the distribution of the finite amount of isotope to be enriched over the different parts of the enrichment system (the theoretical upper limit for the enrichment is the ratio of the total sample mass to the mass of the enriched sample). The net isotopic mass transport of the column determines the time it takes to reach a certain enrichment. Table 2 presents the results of calculations of the enrichment to be expected for several different single column systems. Because a serious discrepancy exists between calculated and observed enrichments (Grootes and Stuiver, 1979) we assumed in our calculation that the same measured effective values for the thermal diffusion transport coefficient (≈0.8H) and the mixing transport coefficient (≈1.7K) also apply for the smaller diameter columns. Although such empirical corrections will

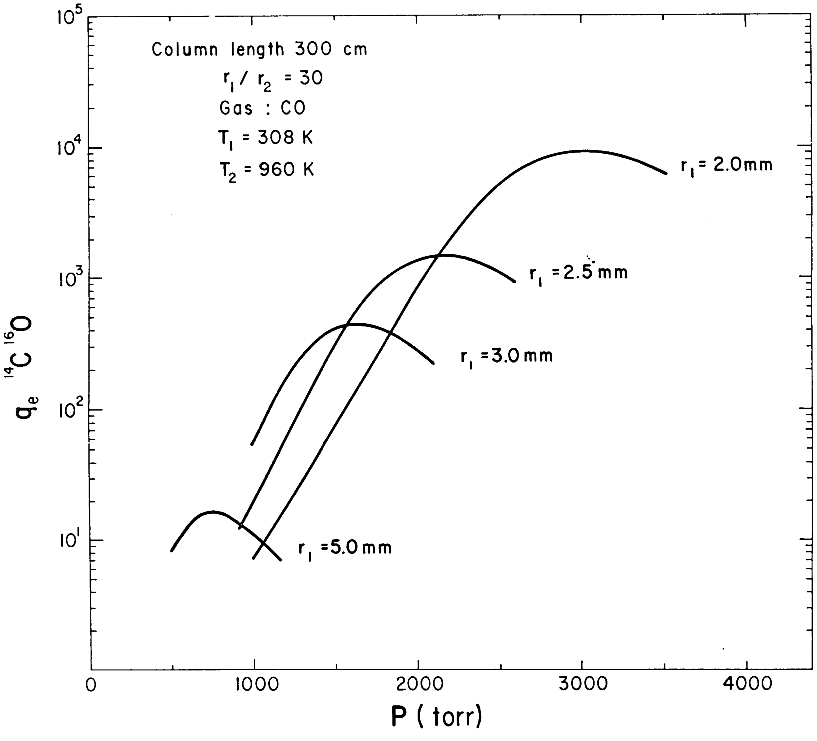

Fig 1. Equilibrium separation factor q_e for $^{14}C^{16}O$ in a hot wire thermal diffusion column as a function of column and wire radii r_1 and r_2 and of pressure p. The subscripts 1 and 2 here indicate the cold column wall and hot wire surface, respectively.

TABLE 2

Enrichment expected for different single column systems

System		m_{tot}(gC)	q'_e	t_r(days)	q′ in 3 days	Age gain ~(years)	q′ in 7 days	Age gain ~(years)
$r_1 = 2.0$mm	$r_2 = 0.067$mm	0.5	17.9	4.2	9.7	18,300	14.8	21,600
L = 300cm	p = 3000torr	1.0	28.8	7.2	10.5	18,900	18.4	23,400
		2.0	41.4	10.6	11.0	19,300	20.5	24,300
$r_1 = 2.5$mm	$r_2 = 0.083$mm	0.5	15.9	3.3	9.9	18,400	14.1	21,300
L = 400cm	p = 2200torr	1.0	27.4	6.3	11.1	19,300	18.8	23,600
		2.0	42.8	10.3	11.6	19,700	21.7	24,700
$r_1 = 3.0$mm	$r_2 = 0.10$mm	0.5	12.0	2.3	9.1	17,700	11.5	19,600
L = 400cm	p = 1700torr	1.0	19.0	4.0	10.4	18,800	15.8	22,200
		2.0	26.7	6.0	11.1	19,300	18.7	23,500

Hot wire temperature $T_2 = 960$ K, cold wall temperature $T_1 = 308$ K.
Ratio $r_1/r_2 = 30$ for all columns; $H_{eff} = 0.8$ H; $K_{eff} = 1.7$ K.
Amount of enriched sample $m_+ = 10$mg of C ~ 23mg of CO.

yield more realistic results, the closeness of the approximation achieved will depend on the pressure dependence of the extra contribution to K.

The amount of enriched sample postulated for calculation of the results in table 2 (10mg) is large enough to yield a sample for the accelerator and to allow a mass spectrometric measurement of the enrichment of the isobaric molecule $^{12}C^{18}O$ to determine the ^{14}C enrichment. The column length is chosen such that the mass ratio of total sample to enriched sample is the most important factor determining the enrichment.

A proposed enrichment system is shown in figure 2. The choice of the column diameter and length will probably be different for different laboratories and will depend upon such practical considerations as whether a tube of the right inner diameter that is sufficiently uniform

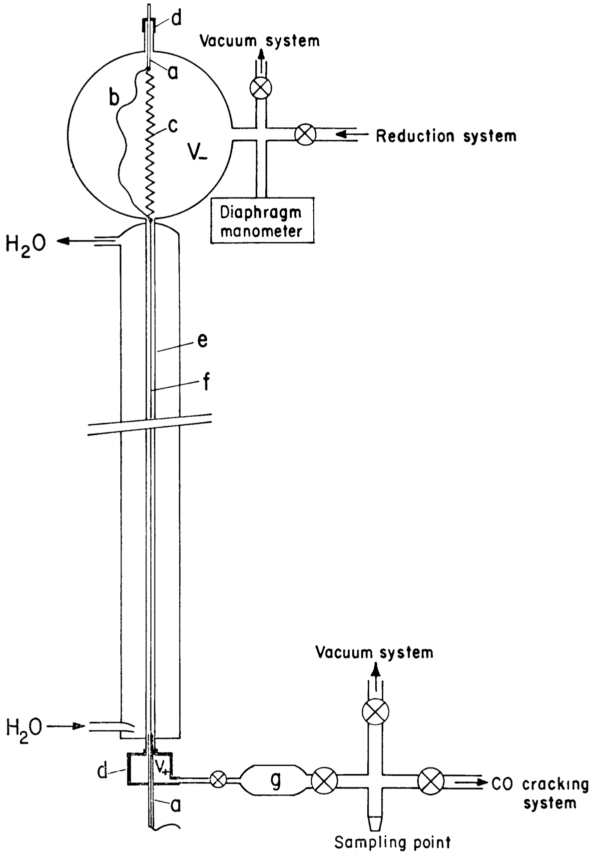

Fig 2. A small sample thermal diffusion enrichment system for CO. The volume V_- has to be chosen such that the system will be filled to the right pressure by the amount of gas used. Dimensions are in table 2. a–copper capillary; b–flexible copper wire; c–steel spring; d–kovar; e–pyrex glass diffusion column with cooling jacket; f–Pt-Ir (80-20%) wire; g–expansion volume for taking enriched samples; V_-–reservoir; V_+–enrichment volume.

and a matching, homogeneous Pt-Ir (80 to 20 percent) wire can be obtained and what pressures can still safely and easily be handled.

As can be seen from table 2, we may expect, for this type of system requiring 0.5 to 2g of carbon, a gain in age range of 18,000 to 19,000 years in 3 days and 20,000 to 24,000 years in 7 days of enrichment. This gain in age is not very sensitive to variations in operating conditions such as pressure or temperature, since a large decrease in enrichment from, eg, 15 to 10 corresponds only to a decrease in age gain from 21,800 to 18,500 years. If a 2mg rather than a 10mg enriched sample were taken, an additional gain in age range of ≈ 3000, ≈ 2500 and ≈ 1800 years would be obtained for the $r_1 = 2.0$, 2.5 and 3.0mm columns, respectively. However, it would then be more difficult to measure the $^{12}C^{18}O$ enrichment since after measurement the residual sample would have to be collected and used for ion counting.

Although, of course, the precise effects of the system configuration and the higher pressure are unknown, it seems safe to predict that a system of this type will extend the age range by at least 20,000 years. When sufficient further progress has been made with accelerators in regard to the precision and reproducibility of sample comparisons by ion counting and when isotopic enrichment is used, the technical dating range with accelerators may well reach 100,000 years as suggested in the first accounts of the new technique (Muller, 1977).

This does not mean, however, that meaningful dates in this age range can be obtained. This will ultimately be determined by the availability of uncontaminated samples. The fraction of the original ^{14}C left in a 100,000 year-old sample is 3.9×10^{-6} (based on the conventional ^{14}C half-life of 5568 years). To obtain meaningful measurements, the amount of recent carbon that entered the original sample, 1) *in situ* in the soil through the action of percolating groundwater, plant rootlets or soil organisms, 2) during sampling, transport and storage and, 3) during handling and processing in the laboratory, should be much smaller than 4×10^{-6}.

The main problem of contamination is not so much the absolute amount (4×10^{-6} would give an error of one half-life or only ≈ 6 percent in a sample 100,000 years old) as the uncertainty in the amount and activity of the contaminants and the possibility that a finite age will be obtained for a sample, that may be millions of years old.

It has been proven by proportional counting combined with thermal diffusion ^{14}C enrichment that, with careful sample selection and treatment, contamination levels permitting ^{14}C dates up to 75,000 years can be obtained (Grootes, 1977; 1978; Stuiver, Heusser, and In Che Yang, 1978), but the lack of contamination has to be established for 100,000 year-old samples.

For such old samples, the cross contamination among different samples mounted on the same sample assembly ("cross talk") in the accelerator ion source must also be kept extremely small. Much remains to be done here.

TABLE 3

A. Comparsion of carbon samples prepared for Van de Graaff Cs sputter ion source

Type of source	$\frac{^{12}C^{-}\text{ beam source}^{*}}{^{12}C^{-}\text{ beam graphite}}$
graphite**	1.0
charcoal from wood	≈ 0.045 (0.01-0.30)
charcoal from excavation	≈ 0.015
cast iron	0.05 -0.16
carbon/iron mixture	0.08 -0.12
Ca CO_3	0.015-0.035
pencil no. 1	≈ 0.23
anthracite	≈ 0.16
C/KBr	0.02 -0.20
charcoal briquet, pressed, 2700°	≈ 1.0
wood charcoal, pressed, 750-2500°C	0.09 -0.17
cracked C	0.03 -1.0†
cracked C, pressed, 2700°	0.06
3 parts wood charcoal + 1 part coal tar pitch, pressed, 1000° (carbonized)	0.06
3 parts charcoal + 1 part pitch, pressed, 1000°, 2500° (graphitized)	0.4 -1.0
Ta blank in 10 min	0.11 → 0.018

* Measured in a removable Faraday cup at the low-energy (LE) end of the accelerator.

** Output ranges from 5 to 20μA depending on beam desired. Controlled by Cs temperature.

† Three sources started with ≈0.5, increased for a few minutes (up to 0.67) then fell off to ≈0.3 after 10 min; one started at 1.0 and dropped to 0.3; changing the position gave back 0.8 immediately. Effects of small differences, in source geometry are not taken into account.

B. Typical sputter ion source performance with beryllium
Ion currents from commercial Be metal* source

0_2 gas pressure	Inflected ion	Current to LE cup** (nA)	Current to HE cup† (nA)	Current to IMC‡ (nA)	Current to DE cup# (nA)
zero	^{9}Be—	3.3	0.5		
	10—(^{9}Be^{1}H—+,, ,)	10			
	25—(^{9}Be^{16}O—+,, ,)	50	(with above yields)		
		60	78	2.3(^{9}Be^{+3})	(not measured)
2.5×10^{-6} torr	25—(^{9}Be^{16}O—+,, ,)	150	275	10.5(^{9}Be^{+3})	(not measured)
		Higher Cs oven temperatures, stabilized source, typical large beams			
2.5×10^{-6} torr	25—(^{9}Be^{16}O—+,, ,)	600-800	800-1000	40-60 (^{9}Be^{+3}) with second stripper¶	30-40 (^{9}Be^{+3}) 6-8 (^{9}Be^{+4})

* Brush Wellman S-200-#, Type I, 0.060 inches thick.

** A removable Faraday cup at the low-energy (LE) end of the accelerator which measures ion beams analyzed by the inflection magnet only.

† A removable Faraday cup at the high-energy (HE) end of the accelerator.

‡ A removable collecting electrode which meaures ion beams after 90° deflection and analysis by the analyzing magnet.

\# A Faraday cup used for beam monitoring and normalization, located just beyond the final ^{14}C detector position.

¶ A C foil (1,005μg/cm^2) used for differential energy degradation of ^{10}Be and ^{10}B. This enables complete magnetic separation of ^{10}Be^{+4} and ^{10}B^{+4}.

Thus, although a ^{14}C dating range of up to 100,000 years is probably technically feasible, contamination may be the major factor limiting the actual dating range for ^{14}C.

Sample preparation for an accelerator

Use of the FN tandem Van de Graaff accelerator of the Nuclear Physics Laboratory (NPL) at the University of Washington for ion counting has been under study and development since the spring of 1977 (Farwell and others, 1980). In the summer of 1978 a joint project of the NPL and the QL was started to measure ^{14}C/^{12}C and ^{10}Be/^{9}Be ratios. The preparation of samples for these measurements is reported here.

Sample preparation for an electrostatic accelerator should meet the following criteria:

1) be feasible on a small scale, using only milligram samples to take full advantage of the sensitivity of the method,
2) be quantitative so that no isotopic fractionation takes place,
3) be carried out in a closed system to minimize the risk of contaminating the sample with foreign carbon (or beryllium),
4) produce a sample that, when placed in the ion source of the accelerator, yields an intense beam of ions that is stable for several hours.

This requirement can be relaxed if a comparison method with frequent interchange of a standard with an unknown source is used, or if adequate continuous monitoring of source output can be achieved.

We first measured how much ^{12}C and ^{9}Be beam could be obtained from different source materials under different conditions in our Cs sputter ion source. For carbon, the strongest beams were obtained with graphite sources; for beryllium, the largest yields were given by Be metal sources in the presence of oxygen ($\approx 2.5 \times 10^{-6}$ torr). Typical ion yields for sputter source operation with commercial beryllium metal are given in table 3B. While comparable yields were obtained with evaporated metal Be sources (see below), the beams from pressed BeO were at least an order of magnitude smaller. In table 3A, we give the ^{12}C^{-} ion beams obtained for other carbon source materials and conditions, normalized to the yields from graphite. Generally, the beams from other sources are at least 5 to 10 times smaller. Exceptions are the "artificial graphite" and "cracked C" sources.

Cracked carbon sources

The cracked carbon resulted from a scheme to deposit carbon from CO_2 directly on a backing that can be mounted in the ion source. The system is shown in figure 3. The starting material is CO_2 produced by combustion of carbonaceous (pretreated) material. In the system, the CO_2 first is reduced to CO by circulating it by convection through an oven filled loosely with a mixture of glass wool and zinc powder at $\approx$400°C. Reduction is quantitative in less than a half-hour. Subsequently, a glow discharge is started between 2 backing plates of $\approx$1cm diameter that are $\approx$½cm apart (potential difference 400-500 V). In the discharge, CO is decomposed ("cracked") to C + O. The O is carried away with the bulk of the gas by convection and eventually bound by the zinc. The carbon is deposited on both electrodes if AC power is used or on the cathode if we use a DC discharge. A relatively small amount is deposited on the surrounding walls.

Although the discharge cracking of CO will work up to at least 100 torr pressure, the best results are obtained for pressures smaller than 10 torr. The decomposition rate is higher at lower pressures, probably because there is less chance of recombination, and the carbon deposited on the backing forms a more uniform deposit. Since the discharge can be maintained down to pressures of $\approx 150\mu$, the decomposition of the sample is almost quantitative.

The main problem remaining is to obtain a homogeneous carbon deposit localized within a narrowly defined area of the backing and thick enough to provide durability when used in the ion source. So far we have not succeeded. The best beam was obtained for a carbon layer deposited with an AC discharge on two backings. The initial beam was $1.8\mu A$ of $^{12}C^{-}$ (under source conditions where graphite gave $\approx 1.7\mu A$) but the beam decayed with a half-life of about 7 min as the Cs ions burned through the thin carbon deposit.

Deposits have been obtained on the center of a backing with a DC discharge. The discharge, however, was not sufficiently localized and produced a lumpy deposit that gave a poor $^{12}C^{-}$ beam.

Isotopic fractionation was measured by converting the carbon deposit back to CO_2. For the original CO_2, we measured $\delta_{PDB}{}^{13}C = -24.40 \pm$

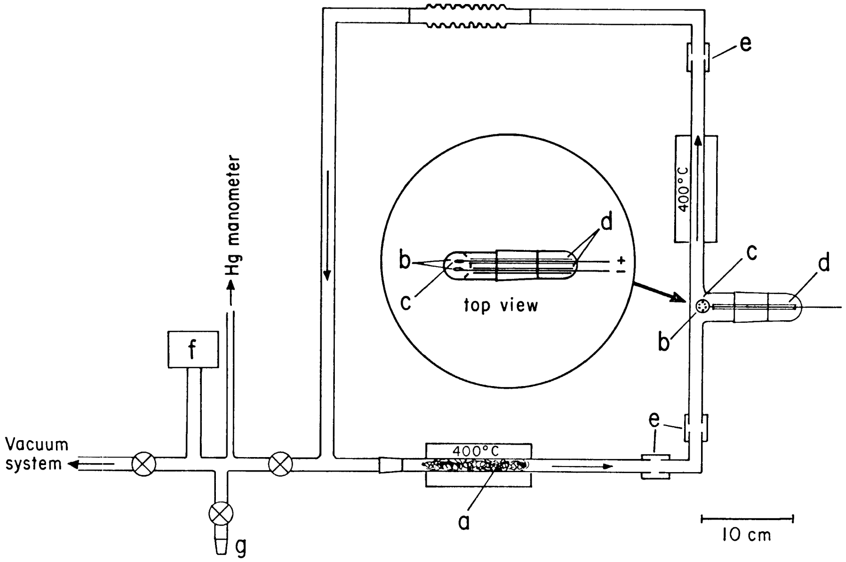

Fig 3. System for reducing CO_2 to C. a–zinc powder on pyrex wool; b–sample backing (Mo, Ta); c–area of glow discharge; d–glass capillary-insulators; e–o-ring vacuum coupling; f–thermocouple gauge; g–connection for CO_2 sample.

0.10‰; after cracking and combustion we found $\delta_{PDB}{}^{13}C = -25.24 \pm 0.11$‰. The effect of isotopic fractionation in the cracking process is, therefore, negligible until a measuring precision of the order of 2‰ has been obtained.

The cracking process described above meets all requirements for a good sample preparation except the sustained high ion output. It also produces material that gives ^{14}C beams relatively free of contaminant ions (Farwell and others, 1980). Further work on CO cracking along the lines used for the RF cracking of acetylene (Purser, Liebert, and Russo, 1980) is in progress.

Other carbon source preparation technique

While the cracking experiments were going on, other ways to process carbon samples to give ion beams comparable to those from graphite were tried at the NPL, one of which proved successful. As a starting material, carbon, obtained by carbonizing wood or charcoal in a stream of nitrogen at ≈1000°C or by cracking CO_2 (see above), was used. This carbon is powdered and mixed with 1/3 of its weight of coal tar pitch. About 15mg of this mixture is pressed into a mold. A number of these molds, arranged such that the pellets are kept under pressure by a strong spring, is then heated slowly to 1000°C in a N_2 atmosphere over a period of 3 hours. After cooling the now firm sample pellets are removed from the molds. Typically, they lose ≈30 percent of their weight in this step. Finally, the pellets are heated slowly to ≈2500°C in vacuum ($\approx 10^{-5}$ torr) for 10 to 15 minutes. This final heating step apparently changes the structure of the carbon in the pellet, because it is only after this treatment that graphite-like $^{12}C^-$ beams can be obtained. The pellets produced by this method give large $^{12}C^-$ beams (up to $20\mu A$ $^{12}C^-$ at the entrance of the accelerator) that remain constant over many hours. Moreover, this step serves to dramatically reduce contaminant ions (see Farwell and others, 1980).

The use of the coal tar pitch means an admixture of, presumably, ^{14}C-free carbon. Experiments indicate that 93 percent to 95 percent of the pitch probably is eliminated by the heating steps. Although admixture of a known amount a few percent of dead carbon does not seriously affect age measurements, the effect of the pitch will have to be studied further if this method of sample preparation is to be used routinely.

Laboratory preparation of beryllium metal sources

For the Be samples, a method was developed to convert BeO, which is the normal end product of Be sample preparations (eg, Merrill, Honda, and Arnold, 1960; Amin, Kharkar, and Lal, 1966), into Be metal. To this end, the BeO is mixed with Mg powder and subsequently heated in a crucible to 800-900°C. The BeO is reduced by the Mg to Be. The Be then evaporates out of the crucible at a higher temperature, about 1300-1400°C, and is deposited in a small central depression of a Ta sample backing placed immediately over the crucible.

Milligram quantities of Be can be handled in this way and several of the Be metal samples thus produced have given ^{9}Be beams equal to those from commercial Be metal for several hours (up to $\approx$60 nA ^{9}Be^{+3} after the analyzing magnet).

Although we still hope to improve our sample preparation methods, and experiments to this end are continuing, we are, at present, able to obtain both carbon and beryllium sources that produce large and stable beams and enable us to explore the application of the NPL Van de Graaff accelerator to ^{14}C and ^{10}Be dating.

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