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PRODUCTION OF LITHIUM CARBIDE FROM VERY SMALL ORGANIC AND CARBONATE SAMPLES FOR LIQUID SCINTILLATION RADIOCARBON ANALYSIS

Summary. The paper describes the system developed in the Radiocarbon Laboratory of Department of Environmental Radiogeochemistry in Kiev. The system is designed for direct obtaining of acetylene from very small samples of organic matter or carbonates. It allows to produce benzene from very small quantities of acetylene (as low as 0.05 g) with the overall chemical yield higher than 92% for organic samples and higher than 96% for carbonates. The developed system is relatively inexpensive in operation and may fill the gap which arises between classical radiocarbon techniques requiring samples containing more that 1 g of carbon and the AMS technique dedicated to milligram-sized samples.

OTRZYMYWANIE KARBIDKU LITU Z MAŁYCH PRÓBEK ORGANICZNYCH I WĘGLANOWYCH DLA DATOWANIA RADIOWĘGLOWEGO METODĄ CIEKŁYCH SCYNTYLATORÓW

Streszczenie. Autorzy opisują system skonstruowany w Laboratorium Radiowęglowym Oddziału Radiogeochemii Środowiska w Kijowie, umożliwiający otrzymywanie acetylenu z bardzo małych próbek organicznych oraz węglanowych w wyniku bezpośredniej reakcji badanej próbki z litem. Całkowita wydajność chemiczna produkcji benzenu jest nie mniejsza niż 92% w przypadku próbek organicznych, a w przypadku węglanów przekracza 96%. Opracowany system jest tani w eksploatacji i pozwala na wypełnienie luki pomiędzy klasycznymi technikami pomiarowymi wymagającymi próbek o masach rzędu kilku gramów węgla a techniką akceleratorową stsowaną do próbek o masach miligramowych.

1. Introduction

Significant progress has been achieved in the techniques and instrumentation over the last three decades of development of radiocarbon dating by liquid scintillation (LS) counting of benzene. The actual trends (Polach, 1992) aim to increase the precision and accuracy of dating results, decrease the minimum mass of organic material necessary for dating with adequate accuracy as well as to expand the range of applications of the LS technique (Noakes et al., 1993). Modern liquid scintillation -spectrometers allow for reliable assessment of radiocarbon concentration in very small benzene samples with volumes as low as 0.3 ml (Polach et al., 1988; Hogg, 1992; 1993; Kaihola et al., 1992; Buzinny, Skripkin, 1995). This possibility may fill the serious gap which arises between AMS method which requires miligrams of carbon and traditional versions of LS and gas counting (GC) methods, which require samples containing more than 1 g of carbon for routine dating with reasonable accuracy. There are numerous practical problems in dating archaeological finds, museum objects or Quaternary sediments where application of „conventional" LS microtechnology may substitute the AMS technique. Recently Zhou et al. (1994) have applied this possibility of the LS technology to dating small organic samples from China.

2. Production of lithium carbide from organic samples

The system of extraction, purification and trimerization of acetylene developed in our laboratory allows to produce benzene from very small quantities of acetylene (as low as 0.05 g) with the overall chemical yield higher than 92%. In the well known and widely used classical methods (Noakes et al., 1963; 1965) of obtaining lithium carbide from wood, peat, collagen, humic acids and other organic matter the samples are first combusted to produce carbon dioxide or charred to obtain elemental carbon. Both ways are time-consuming and require sophisticated equipment and, moreover, significant losses of carbon may occur at these stages. It is known that during charring of most organic substances only 10-35% of carbon is transferred into the form of elemental carbon (depending on the composition of a sample and conditions of pyrolysis) while 65-90% of carbon is lost as it is rejected with the gaseous and volatile pyrolysis products.

In order to produce lithium carbide from micro-samples containing 0.05-1 g of carbon with minimum losses we have developed a technology based on direct reaction of organic sample with lithium in stainless steel ampules with titanium liner. The design of a very simple apparatus used in this technology is shown schematically in Figure 1.

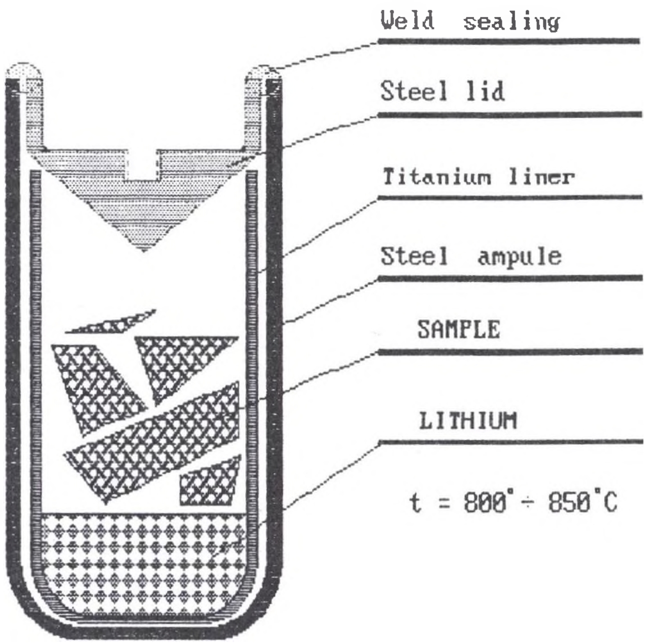

Fig. 1. Apparatus for direct reaction of organic sample with lithium in stainless steel ampules used to produce lithium carbide from micro-samples containing 0.05–1 gram of carbon

Rys. 1. Urządzenie do produkcji karbidku litu z bardzo małych próbek organicznych zawierających 0.05–1 g węgla na drodze bezpośredniej reakcji substancji organicznej z litem

After standard chemical treatment the sample is dried at 120°C, weighed and placed into the ampule together with carefully determined amount of lithium. The ampule is covered with a lid and sealed by welding. The conical bottom of the lid is tightly adjacent to the titanium liner. The set of 10 or more ampules is placed in a stainless steel vessel which is heated to 800°C for 2 hours in a vacuum, argon or air. The process of pyrolysis of organic matter and absorption of gaseous pyrolysis products by melted lithium proceeds concurrently in the ampules. Water, hydrocarbons, alcohols, carbon oxide, carbon dioxide, nitrogen and phosphorus compounds are deposited in the process. Lithium is melted at 170–190°C and begins to react first with water and alcohole vapours. The temperature in the reaction zone increases and absorption of the gaseous pyrolysis products speeds up. In the result of this interaction the mixture of oxide, hydride and lithium carbide is formed. Nitrogen, sulphur and phosphorus form a small quantity of lithium cyanamide, sulphide and phosphide. In 15–20 minutes after beginning of heating, the organic sample is transformed into the mixture of the above mentioned compounds. Further heating leads to redistribution of the dopants (nitrogen, sulphur, phosphorus and partially hydrogen) between lithium and titanium. Decomposition of various compounds of lithium with nitrogen, sulphur, phosphorus and carbon to the elements occurs at temperatures above 800°C. Carbon is the only element which does not change to gaseous phase and remain in lithium. The other elements are absorbed by the titanium liner, forming thermally stable compounds.

3. Production of lithium carbide from carbonates

When obtaining the counting medium from microquantities of carbonates (less than 0.5 g of carbon in a sample) it is vital to minimize the losses of carbon at all stages of chemical treatment. We have developed appropriate technology for obtaining lithium carbide from carbonate samples without preliminary production of CO_2. The process is accomplished in specially designed ampules made of stainless steel and titanium, shown in Fig. 2. A sample is placed at the bottom of the ampule and a titanium liner with lithium is put at the top. The ampule is blown with argon, covered with a stainless steel lid and tightly sealed by welding.

The ampules are marked by engraving and heated in an electric furnace to 850°C for 2 hours. A large number of ampules (10–50) may be heated simultaneously. There is almost no possibility of contamination of carbonate in the ampoules by admixture of external carbon. At 550°C the carbonate begins to decompose and causes rise of partial pressure of carbon dioxide. Simultaneously the reaction of carbone dioxide with lithium is going on what results in establishing of a steady state between release and absorption of carbon dioxide.

The process of carbon transfer from carbonate into carbide do not causes rising of partial pressure of carbone dioxide over 0.5 atm and is completed within one hour after reaching the temperature of 850°C. Additional heating of the ampules for 30 minutes is necessary to form carbide in zones with poor permeability to lithium. The titanium liner does not absorb carbon in the reaction zone at temperature below 850°C. Titanium adsorbs dopants (ie, nitrogen, sulphur, phosphorus) as well as oxygen and hydrogen. It allows to obtain very pure acetylene with high overall chemical yield exceeding 96%. The obtained carbide may be stored in the ampule for a long time without any risk of its decomposition or contamination.

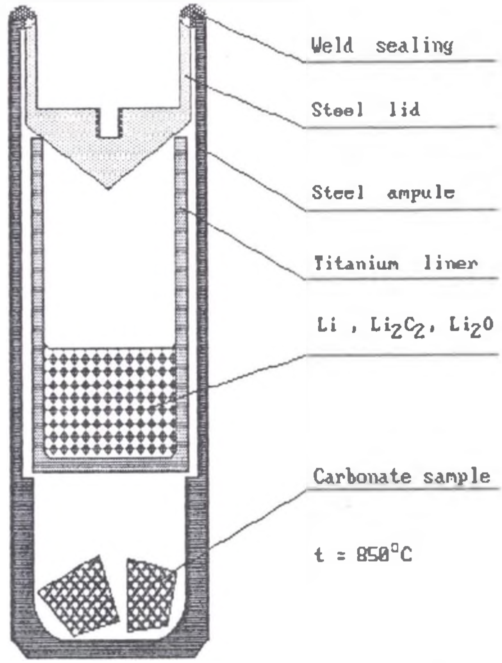

Fig. 2. Apparatus for direct reaction of carbonate sample with lithium in stainless steel ampules used to produce lithium carbide from very small carbonate samples

Rys. 2. Urządzenie do produkcji karbidku litu z bardzo małych próbek węglanów na drodze bezpośredniej reakcji próbek organicznych z litem

4. Conversion of lithium carbide to acetylene

The ampules can be stored for any needed time and opened just before the production of acetylene. To open the ampule a simple tool is used.

Maximum gas presure in the ampule is below 10 atm throughout the whole process. The ampule is designed for maximum pressure of 50 atm at 800°C. In the course of the tests with maximum filling of the ampule with the ingredients there were no cases of explosion of the ampules. The method was tested on samples of different composition using known age samples with wide range of radiocarbon activities. It was found that no systematical age differences and no „memory effect" occur within the limits of measurement error of physical instrument.

5. Summary and conclusions

Implementation of this technique in connection with the modern achievements in the field of LS spectrometers may allow to expand significantly the range of the LS counting. The estimated limits of the developed technology are compared in Table 1 with typical requirements of the classical technology of LS counting. The technology is simple and inexpensive; the relative cost of the ampule is below 1% of the estimated total cost of dating. The technology allows to work with many samples simultaneously and this may result in significant reduction of the time necessary for preparation of single sample and to increase at the same time the overall laboratory output.

Table 1

Comparison of the minimum mass of organic samples required for radiocarbon dating

Material	Present	Conventional
Charcoal	0.15	5
Wood	0.30	10
Bones	3–5	100
Soil (2–5% of organics)	30–50	1000

The developed technology has been tested experimentally at The Radiocarbon Laboratory in Kiev. The results obtained on several samples dated using the classical version of the LS technique are compared with the results obtained on small aliquots of same samples prepared according to described technology. The results are listed in Table 2.

Both kinds of samples were counted on QUANTULUS 1220 LS spectrometer. In counting micro-samples the vials developed by Buzinny and Skripkin (1995) have been used. The results in Table 2 show very good agreement between both sets of radiocarbon dates as well as their good consistency with known historical dates. Finally, it should be mentioned that the developed technology has been recently widely applied in studies of the Ukrainian pre- and protohistory. Several museum objects of high scientific value were dated, including textiles, small wooden artifacts and other samples which may be characterized by very high degree of association with archaeological finds. Two examples of the application of the developed technology to solving specific archaeological problems are presented in papers by Pavlova et al. (1995; this volume) and Panchenko and Kovaliukh (1995; this volume).

Table 2

Comparison of radiocarbon dates obtained using the microsamples prepared according to developed technology with radiocarbon dates of same objects obtained according to conventional technology of benzene production

Site	Historical date	Radiocarbon dates	
		conventional	microsample
Prince Vladimir Town Desiatyna Church	AD 945	1020±55	980±105
Mikhailovski Zlatoverkhi Cathedral	AD 1113	810±55	750±110
Prince's Town, Kiev Blacksmith House	AD 1240	720±60	770±90
Vyshgorod Ancient Settlement	XII Century AD	760±50	810±90

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Streszczenie

Autorzy opisują technologię wytwarzania karbidku litu z próbek organicznych o bardzo małej masie (poniżej 0.1 g węgla) opracowaną w Laboratorium Radiowęglowym Oddziału Radiogeochemii Środowiska Akademii Nauk Ukrainy w Kijowie. Opracowana technologia i służąca do jej realizacji aparatura są proste i efektywne oraz stosunkowo tanie w eksploatacji. Całkowita wydajność chemiczna reakcji prowadzących do uzyskania wyniku końcowego w formie preparatu pomiarowego w postaci benzenu wykorzystywanego do oznaczenia koncentracji izotopu ^{14}C jest nie mniejsza od 92%. Opracowana technologia została sprawdzona przez zasytosowanie jej do wykonania oznaczeń wieku na próbkach muzealnych reprezentujących zabytki średniowieczne ze zbiorów Muzeum Narodowego Ukrainy w Kijowie. Oznaczenia wieku wykonane techniką konwencjonalną na próbkach o masie większej od trzech gramów są w bardzo dobrej zgodności z wynikami oznaczeń wieku wykonanych na mikropróbkach o masie nie większej niż pół grama substancji organicznej. Wykonane dotychczas testy laboratoryjne dowodzą, że użyte do konstrukcji aparatury materiały zapewniajl jej bezpieczną eksploatację oraz brak zauważalnego efektu pamięci.