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RADIOCARBON POTTERY DATING: THE CHEMICAL COMPOUNDS OF ORGANIC FRACTIONS, THE RELIABILITY OF ^{14}C DATES (PRELIMINARY RESULTS)

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Abstract: In recent times, a large number of radiocarbon dates appeared for the Southern Neolithic on the basis of pottery dating because other organic matter has practically not been preserved. There are two organic fractions of pottery useful for dating: food residues and carbon from the pottery matrix itself. Food residues are often dated, but this material is not always preserved and is prone to being removed during the cleaning of the pottery. The clay mass of the pottery contains carbon, often directly visible upon breaking of the pottery. The article focusses on determining the chemical composition of the organic fractions in the pottery and the origin of the carbon. For this aim we used the nuclear magnetic resonance (NMR) method to identify the chemical compounds in the food residue and in the pottery matrix.

As an example we used pottery from the Neolithic sites: Zamost'e (Central Russia) and the Varfolomeevskay sites (Southern European Russia, Low Volga region) from archaeological collections.

The results obtained demonstrate that the food residue and the pottery matrix contain practically the same organic compounds, even if the relative abundances of various compounds are different in these materials. The origin of the carbon from pottery is discussed.

Keywords: Neolithic, pottery, chemical composition, radiocarbon chronology, nuclear magnetic resonance.

1. INTRODUCTION

Wood, charcoal, bone and soil are most often used for radiocarbon dating. It is not unusual, however, that archaeological sites do not yield any wood, charcoal, or any other organic material suitable for radiocarbon dating. This happens particularly often in southern regions where environmental conditions preclude the preservation of organic materials. In such cases, the bone collagen can also be destroyed, making radiocarbon dating problematic. Furthermore, it is often difficult to establish confidently the association of the material dated with the archaeological event of interest; this can lead to discrepancies between the archaeological and radiocarbon dates.

A possible solution is the direct measurement of organic matter included into the archaeological artefact. Such an artefact can be pottery. Food residue on the pottery can provide evidence of the time when the pottery

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was used, but such a residue is not always preserved or formed. Neolithic archaeological sites usually contain large amounts of pottery, which is usually used for the archaeological attribution of the site. The age of a pottery assemblage is commonly estimated as the radiocarbon age of organic matter samples obtained from objects which are deemed to be synchronous with the pottery (hearths, seeds, wooden structures, etc.). As noted above, the association of such objects with the pottery can be difficult to be established confidently. Hence, direct measurements of the organic carbon derived from the pottery matrix have been repeatedly attempted since the 1950s. Bonsail *et al*. (2002) provide a useful review of the methods of pottery dating. The origin of the organic matter is the main problem in the direct dating of pottery. In particular, it has to be clarified what organic compounds contain the datable carbon. We present our results on the identification of the carbon-containing materials within the pottery matrix using the nuclear magnetic resonance (NMR).

2. METHODS

In the current work, pottery from Neolithic sites has been studied. The map of sites studied is presented in **Fig. 1**. The base principle of the method used is described bellow.

Nuclear magnetic resonance is widely used to identify organic compounds in a sample (Ionin and Ershov, 1970; Ionin *et al*., 1983; Harris and Wasylishen, 2010). In recent times, this method has been applied for archaeological studies (Lambert *et al*., 2000; Barded *et al*., 2002).This method is based on the detection of signals from nuclei placed in a strong magnetic field and irradiated with radio-frequency waves. In this study we applied the NMR spectroscopy of ^{1}H and ^{13}C nuclei. The ^{1}H and ^{13}C NMR spectra can reveal the presence of esters of fatty acids, alcohols and other organic compounds. Since the method is sensitive to the presence of double bonds in organic compounds, carbon of geological origin can be confidently identified.

We used the Bruker AVANCE 500 NMR spectrometer (with the working frequency of 500 MHz for ^{1}H nuclei and 126 MHz, for ^{13}C nuclei) to analyse the solutions extracted from both food residue on, and the charcoal within Neolithic pottery samples. A black, charcoal-like layer can be easily seen within freshly broken pottery fragments (**Fig. 2**). The chemical composition of this organic matter and that of the food residue were analysed separately. The pottery fragments and the food residue were powdered, and the organic compounds were extracted by dissolving the powder in hexane. Hexane was then removed and the residue was dissolved in deuterated chloroform ($CDCl_3$). The solution was then NMR analysed for ^{1}H and ^{13}C nuclei. NMR spectral lines were identified by comparison with reference compounds spectra, including olive oil for the lines of triglycerides, cetyl palmitate $CH_3(CH_2)_{14}C(O)O(CH_2)_{15}CH_3$ and decyloleat

Fig. 1. *The Neolithic sites of the Southern and the Low Volga river basin investigated:*
(1) Racushechny Yar,
(2) Matveev Kurgan,
(3) Kairshak I–III,
(4) Kugat IV,
(5) Tektensor I, III,
(6) Burovaya,
(7) Varfolomeevskaya,
(8) Lebyazhinka,
(9) the Yelshanian group of sites,
(10) Chekalino IV,
(11) Maksimovka,
(12) Ivanovskoe,
(13) Dzangar,
(14) Il'inka,
(15) Zamost'e.

$CH_3(CH_2)_9OC(O)(CH_2)_7CH{=}CH(CH_2)_7CH_3$ for esters; octyl ether $[CH_3(CH_2)_7]_2O$ for ethers; 1-octadecanol $[CH_3(CH_2)]_{17}OH$ for fatty alcohol signals; stearic acid $[CH_3(CH_2)]_{16}COOH$ as a fatty acids representative; octadecan (paraffin $CH_3(CH_2)_{16}CH_3$); and beeswax. To record the spectra, these compounds were also dissolved in $CDCl_3$.

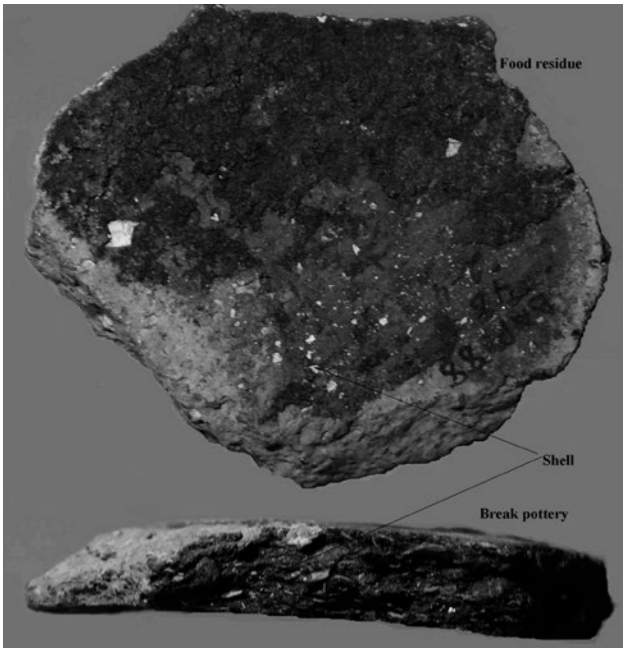

Fig. 2. *The profile of the pottery fragment from the Varfolomeevskay Neolithic site.*

The relative content of organic compounds in the samples can be determined by the intensity of the spectral lines arising from double bounds (I – the chemical shift δ=5.35), as well as those from the triglycerides of unsaturated fatty acids (II – δ_{CHO}=5.30, δ_{CH2O}=4.32 and 4.15,), esters (III – $\delta_{CH2OC(O)}$=4.06 and 4.30), alcohols (IV – δ_{CH2O}=3.64), fatty acids (V – $\delta_{CH2C(O)OH}$=2.25÷2.40) and ethers (δ_{CH2O}=3.38; usually only traces of these can be found). In addition, various aromatic compounds were found in the solutions (VI – δ_{CH}=6.8-7.8; **Figs. 3-4**). Intensive signals around 0.6-2.2 ppm are related to protons of the aliphatic chains of compounds mentioned above.

3. RESULTS

Methods of ^{14}C dating of carbon-containing materials from pottery have recently been developed in the radiocarbon laboratory in Kiev using the conventional technique (Skripkin and Kovaliukh, 1998; Zaytseva *et al.*, 2009). Pottery is one of the most suitable materials for dating because of this artifact is closely associated with archaeological events. It plays a particularly important role in the absolute chronology of the Neolithic in the Southern regions of Russia, including Northern Caucasus and the Caspian Sea region. The origin of the carbon-containing materials in the pottery can be problematic, and it is important to verify if those materials are directly related to the archeological context. The situation with the food residue is much simpler as this material is certain to reflect the time when the pottery was in use. How-

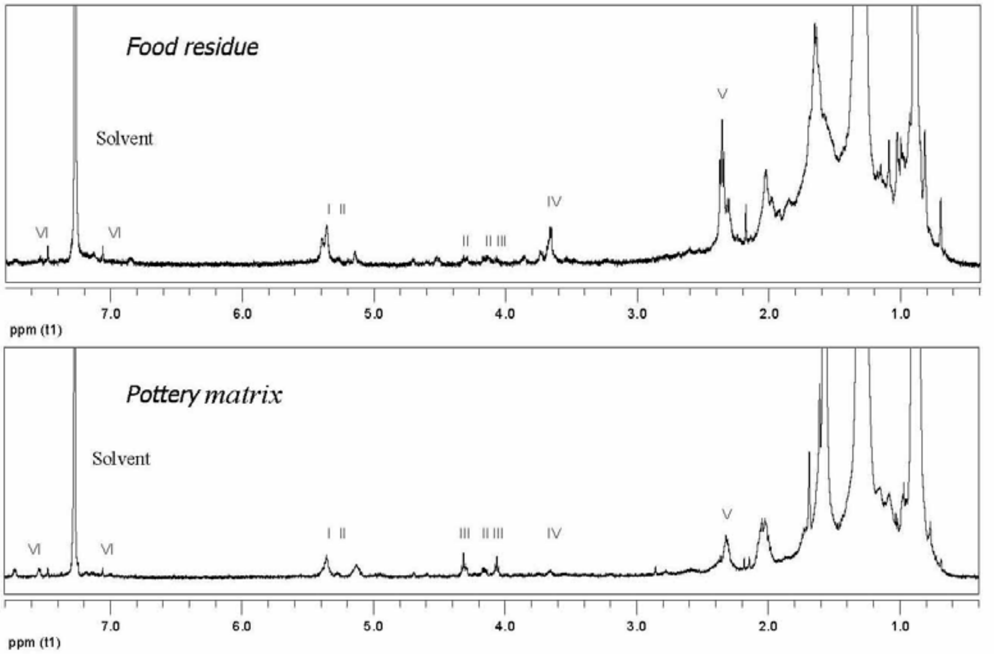

Fig. 3. *The ^1H NMR spectra of the components of the food residue and pottery of the Zamost'e Neolithic site. I: compounds with double bounds; II: triglycerides of fatty acid esters; III: ethers; IV: alcohols; V: fatty acids and ethers; VI-VIII: various aromatic compounds.*

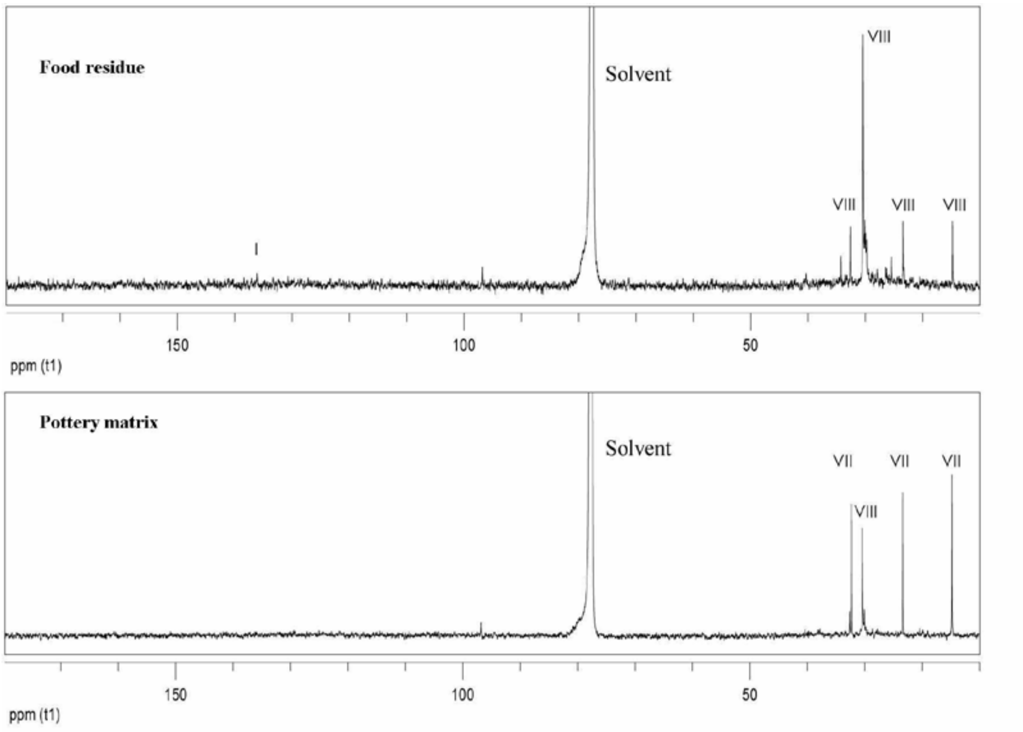

Fig. 4. *The ^{13}C NMR spectra of the components of the food residue and pottery of the Zamost'e Neolithic site. I: compounds with double bounds; II: triglycerides of fatty acids esters; III: ethers; IV: alcohols; V: fatty acids and ethers (δ_{CH2O}=3.38); VI-VIII: various aromatic compounds.*

ever, such a residue is rather rare, in part because it often used to be removed during the clean-up of the samples, e.g. to reveal ornamental patterns. This makes the direct dating of the pottery an especially attractive alternative. However, the carbon-containing materials within the pottery matrix can be of geological and other origin, which we will consider later. Of course, at first the ^{14}C dates were obtained from different fractions of pottery: food residue, charcoal into the pottery matrix. Here we compare the ^{14}C dates from the charcoal inside the pottery (pottery matrix), to those from the food residue on it, as well as from charcoal from cultural layers, bone remains and wood. For this purpose, we used pottery samples collected from the Neolithic sites of the Russian regions shown in **Fig. 1**.

The break fragment of pottery from the Tektensor site is shown in **Fig. 2**.

As known, shells were added to the clay mass to improve this quality (Bobrinsky, 1999; Vasilieva, 2009). Particularly this approach was spread in the Southern regions of Russia (Bobrinsky, 1999; Vasilieva, 1999; 2009).

The main source of carbon in pottery is oozy clay, peat, shells, plant remains and other materials used as temper to improve the technological characteristics of the pottery. To test the reliability of the direct dating of these materials embedded in the pottery matrix, microscopic shell pieces (typical size of a few microns) were manually extracted from the pottery matrix of a sample from the Tektensor site in the Caspian Sea region (**Table 1**).

In order to quantify the reservoir effect, we performed the following comparisons. The shell inclusions were AMS dated at the radiocarbon laboratory of Uppsala University (Sweden). The remaining pottery mass was treated with hydrofluoric acid to eliminate any carbonates. The carbon remaining was then also AMS dated in the same laboratory. Another parameter measured was the stable isotope ^{13}C content, expressed below in terms of:

$$\delta^{13}C = \left[\frac{\left(\frac{^{13}C}{^{12}C}\right)_{Sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{PDB}} - 1\right]\cdot 1000‰ \qquad (3.1)$$

The age of the shell inclusions was determined as 7235 ± 45 ^{14}C BP with δ^{13}C= −13.3‰ (Ua-35226). The age of the carbon remaining after the acid treatment is 6695 ± 40 ^{14}C BP, with δ^{13}C= −27.7‰. The pottery fragments were further separated into an inner layer ('the 'terracotta', red-coloured portion) and the outer layers (of a darker colour). The 'terracotta' layer is free of carbon. The ^{14}C age obtained for the carbon-containing part was determined as 6695±40 ^{14}C BP, with δ^{13}C= −27.7‰ (Ua-35227). This age is in perfect agreement with that ob-

Table 1. *^{14}C dates from different fragments of the clay mass of pottery from the Tektensor Neolithic site, Caspian Sea region (Astrakhan district, Southern Russia; Zaytseva* et al.*, 2009). Dates were calibrated with using OxCal programme v 4.1.7 (Bronk Ramsey, 2009) and calibration curve IntCal09 (Reimer* et al.*, 2009).*

Lab. Index	Material	^{14}C Age, (BP±1σ)	δ^{13}C (‰, VPDB)	Cal Age (95.4%)
Ua-35226	shells from pottery	7235±45	-13.3	6220-6020
Ua-35227	charcoal pottery	6695±40	-27.7	5710-5530
Ki-14137	pottery, entire sample	6630±80	–	5720-5470

tained at the Kiev Laboratory with the liquid scintillation techniques: 6630±80 ^{14}C BP (Ki-14137). Thus, one can assume that the value of the reservoir effect is about 500 years.

It remains to determine which carbon-containing compounds are contained in the food residue and in the clay mass of pottery. The following carbon-containing compounds can be present in the clay mass of pottery:

1) Carbon of the organic matter in the clay, which has geological origin; its age can be reasonably expected to be much older than that of the pottery.
2) Carbon derived from temper (grass, straw, chaff, dung, ground shells, etc.); its age should be contemporaneous with that of the manufacture of the pottery. However, the reservoir effect has to be allowed for in the case of shells.
3) Carbon absorbed from fuel during pottery firing in the kiln.
4) Carbon absorbed from the surrounding soil.

To determine the chemical compounds in the pottery we used the NMR methods. As the samples for our study we used the Neolithic sites from different regions of Russia: forest and steppe zones.

Suitable samples originated from the Zamost'e Neolithic site in the Central Part of European Russian Plain, Moscow Region, shown in **Fig. 1**, which is located in the forest zone and so the finds represent wood, charcoal, peat, as well as pottery with food residue. ^{14}C dates for this site, taken from Timofeev *et al.* 2004 and Dolukanov *et al.*, 2009 are presented in **Table 2**.

The NMR spectra of food residue and carbon-containing material of the pottery clay mass for the Zamost'e samples are presented in **Figs. 3** and **4**. The ^{1}H spectra (**Fig. 3**) reveal the presence of similar, rather complex chemical compounds in both materials. Among such compounds are those with double bonds (C=C), ethers, alcohols and fatty acids, as well as benzene derivatives. These compounds are more abundant in the food residue than in the pottery itself: the total organic mass content in the food residue is 40 times larger than in the pottery clay mass. The ^{1}H NMR spectra indicate that the food residue contains other complex compounds which are as yet difficult to identify.

The pottery matrix demonstrates the high content of ethers (δ = 4.06 ppm and 4.30 ppm (**Figs. 3-4**)) which can originate from vegetable waxes. The ^{13}C spectra of the food residue and pottery are visibly different (**Fig. 4**). While the pottery spectra, accumulated after 10 hours of measurement, show only weak signals of the residual hexane (VII) and paraffin (VIII), the spectra of the food residue contain more lines, including those similar to unsaturated (double-bond) compounds in the ^{1}H spectra. The presence of the compounds with the double bonds (C=C) testifies that the organic compounds in both pottery matrix and food residue cannot be of geological origin because during the long time of preservation these bounds disappeared.

Table 2. *^{14}C dates of the Zamost'e Neolithic site (Moscow region,). Dates were calibrated with using OxCal programme v 4.1.7 (Bronk Ramsey, 2009) and calibration curve IntCal09 (Reimer* et al.*, 2009).*

Lab. index	Material	^{14}C Age (BP±1σ)	Cal Age (95.4%)
GIN-6198	peat	6680±100	5790-5460
GIN-6557	peat	6850±60	5880-5630
GIN-6564	peat	7050±40	6010-5840
GIN-7985	peat	6290±40	5370-5200
GIN-7988	peat	7200±90	6250-5890
GIN-7986	wood	7000±70	6010-5740
Ki-15031	charcoal	6730±120	5890-5470
Ki-15030	food residue	6440±120	5630-5080
Ki-15032	food residue	6300±130	5520-4940

According to the NMR spectra one can identify the following organic compounds:

- Compounds with double bounds (I), having chemical shifts $\delta_{CH2} = 5.35$ ppm,
- Triglycerides (II): $\delta_{CH2O} = 4.32$ and 4.15 ppm, $\delta_{CHO} = 5.30$ ppm
- Esters (III), having chemical shifts $\delta_{CH2OC(O)} = 4.30$ and 4.06 ppm
- Alcohols (IV), with chemical shift $\delta_{CH2O} = 3.64$ ppm
- Fatty acids (V), chemical shift $\delta_{CH2C(O)OH} = 2.25 \div 2.40$ ppm and ethers, chemical shifts $\delta_{CH2O} = 3.38$ ppm
- Various aromatic compounds, with chemical shifts $\delta_{CH} = 6.8–7.8$ ppm (VI).

Other Neolithic sites in which food residues and clay mass could be studied is the Varfolomeevskaya site located in the Lower Volga river basin, Saratov oblast (**Fig. 1**). This is a multilayer site from the early Neolithic up to the Eneolithic period (Vybornov, 2008; Vasilieva, 2009). For this site numerous ^{14}C dates were produced mostly from pottery, because other organic materials (wood, charcoal, bone) were practically lacking. Most of the ^{14}C dates were published by Zaytseva *et al.* (2009). Before then, the capacity of ^{14}C dates produced for the Neolithic sites of the Southern regions of Russia were obtained and presented in the monograph Vybornov (2008).

Now we obtained new ^{14}C dates employing the AMS technique – these dates are presented in **Table 3**.

The NMR spectra of the food residues and pottery matrix from this site are presented in **Figs. 5-6**.

The ^{1}H spectra reveal the presence of rather similar, complex chemical compounds in both materials (**Fig. 5**). In the spectra of the food residue we can observe the intensive signals of methylene groups (CH_2) of the fatty alcohols (IV), δ=3.64 ppm and the CH groups of the aromatic bonds δ=8.22 and 7.53 ppm (VI). These lines can be attributed to the derivates of benzoic acid. Besides, there are the intensive signals at δ=8.10 ppm and 4.69 ppm, which can be attributed to the derivates of terephthalic acid.

The ^{13}C spectra of these fractions are presented in **Fig. 6**. Considering the possible compounds, these spectra correspond to the spectra of ^{1}H with small differences. Thus, if the ^{13}C spectra of the pottery matrix are only the weak signals of paraffin (alkanes), in the spectra of the food residue additional signals of others organic compounds are observed, among this fatty alcohols (δ_{CH2O}=63.7 ppm) and aromatic compounds (δ_{CH}=130.4 ppm). In general, the spectra of the food residue and the pottery matrix look like concerning these chemical lines.

4. DISCUSSION

It is interesting that the NMR spectra for ^{1}H and ^{13}C of the Varfolomeevskaya and Zamost'e sites differ for the food residue and pottery matrix reflecting the particularities of the chemical composition. In spite of the Zamost'e, in the ^{1}H spectra of the food residue of the Varfolomeevskaya site one can observe the intensive signals of the methylene groups (δ=3.64 ppm), fatty alcohols and the signals of aromatic compounds (δ=8.22 and 7.53 pm). Besides, there are intensive signals in the area 8.10 and 4.69 pm, which can be related to the derivates of the terephthalic acids. In the spectra of the pottery matrix the content of fatty acids is higher than in the Zamost'e sample. Unlike the Zamost'e samples, in the pottery matrix of the Varfolomeevskay site there are signals of the mono- and diglycerides which can be obtained by hydrolysis of triglycerides. But, if in the spectra of the pottery matrix only weak signals of paraffin are present, in the spectra of

Table 3. *^{14}C dates for the Varfolomeevskaya site. Dates were calibrated with using OxCal programme v 4.1.7 (Bronk Ramsey, 2009) and calibration curve IntCal09 (Reimer* et al.*, 2009).*

No.	Varfolomeevskaya site	Lab Code	Material	^{14}C Age (BP±1σ)	Cal Age (95.4%)
1	Varfolomeevskaya, layer 3	Ki -14110	Pottery carbon	7080±80	6090-5750
2	Varfolomeevskaya, layer 3	Ki - 14144	Pottery carbon	7120±90	6220-5810
3	Varfolomeevskaya, low layer	GIN-6546	charcoal	6980±200	6250-5510
4	Varfolomeevskaya, depth 170-180 cm	Ua- 41360	Food residue	7034±41	6010-5810
5	Varfolomeevskaya, depth 90-100 cm	Ua-41361	Food residue	6544±38	5620-5390
6	Varfolomeevskaya, charcoal from the hearth	Ua-41362	Food residue	6693±39	5710-5530

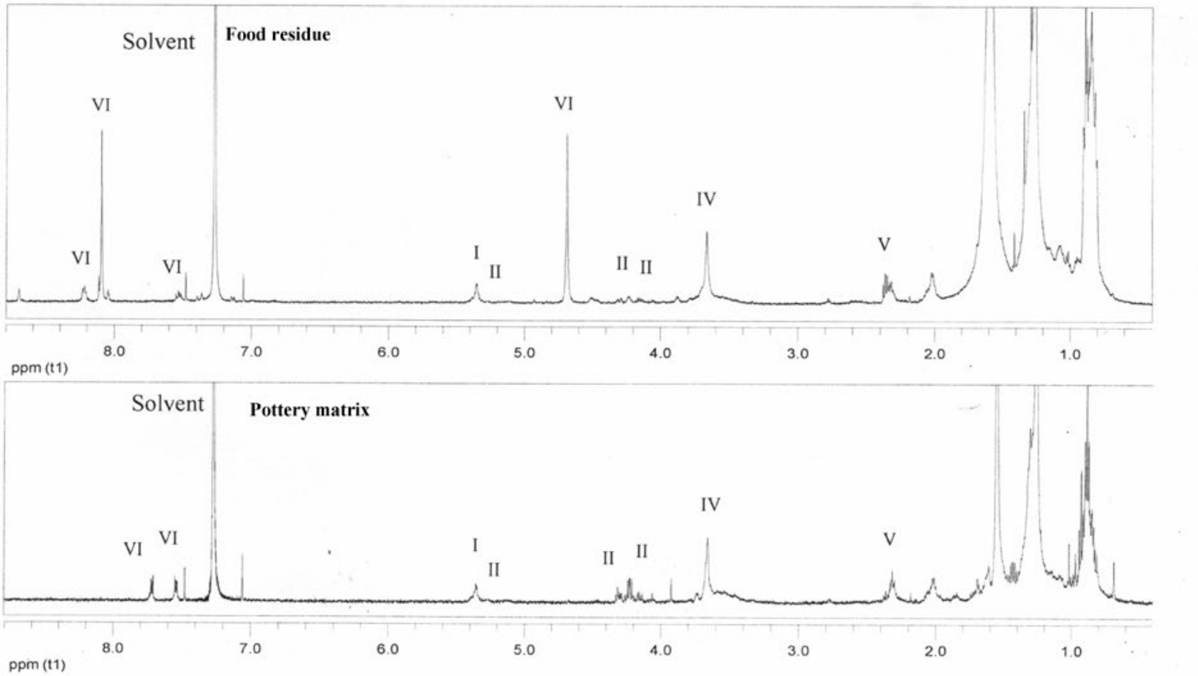

Fig. 5. *The ^{1}H NMR spectra of the components of the food residue and pottery of the Varfolomeevskaya Neolithic site. I: compounds with double bounds; II: triglycerides of fatty acid esters; III: ethers; IV: alcohols; V: fatty acids and ethers; VI-VIII: various aromatic compounds.*

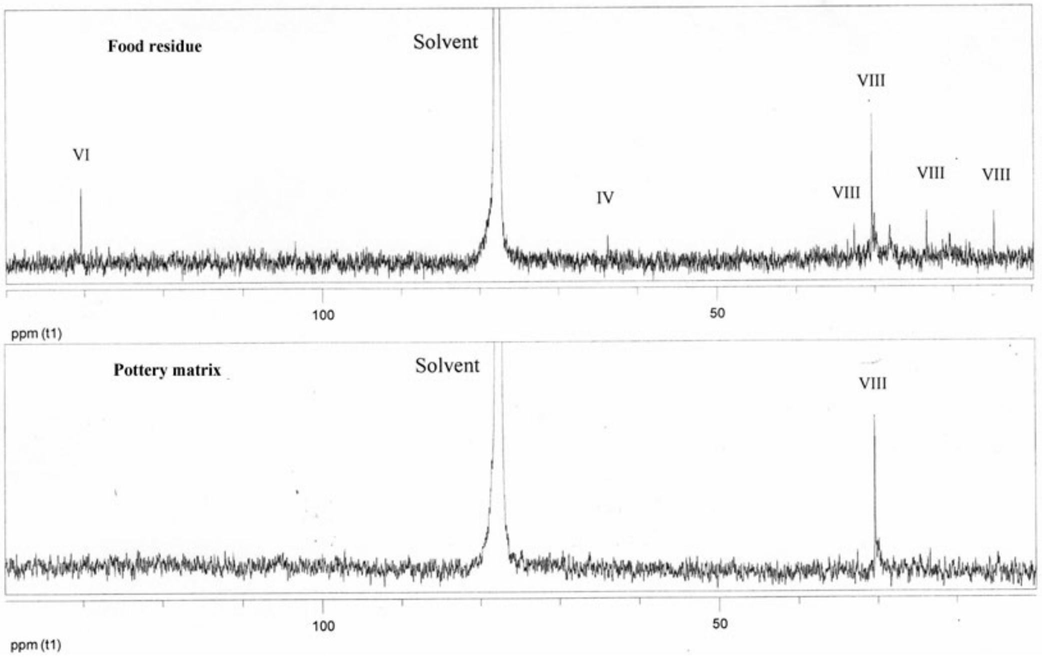

Fig. 6. *The ^{13}C NMR spectra of the components of the food residue and pottery of the Varfolomeevskaya Neolithic site. I: compounds with double bounds; II: triglycerides of fatty acid esters; III: ethers; IV: alcohols; V: fatty acids and ethers; VI-VIII: various aromatic compounds.*

the food residue there are signals of other compounds including fatty alcohol (CH_2 O, δ=63.7 pm) and aromatic compounds (δ=130.4 pm). Undoubtedly these particularities are connected with the method of the pottery marking and admixtures in the clay mass.

It is very important to understand the origin of the organic materials within the clay mass of pottery to know the approaches used in manufacture ancient clay mass. There are several studies focused on the components used for pottery manufacture (Bobrinsky, 1999; Vasilieva, 2009; Tokarenko, 2005). It is well known that different organic materials were used to improve the plastic properties of the clay mass. Besides, sapropel and ooze from lake deposits could be used to form the molding mass (Bobrinsky, 1999). This technique was typical for the southern regions of Russia (Vasilieva, 2009). Sapropel and ooze are cahracterised by complicated structure and biological nature. Their main organic components are humic acids (Sherysheva *et al*., 2009; Dmitruk *et al*., 2009). The composition of humic acids was studied by different methods including IR and NMR spectrometry (Popov, 2004; Gostischeva, 2006). According to these analyses, the molecule of humic acids consists of different groups such as C-O, CO-OH (carbonyl, carboxyl groups), alkanes, aromatic compounds and others (Orlov, 1990; Dmitruk *et al*., 2009). Most probably the compounds from the ooze and sapropel used for pottery manufacture are found in the NMR spectra of pottery. In both cases (the Zamost'e and Varfolomeevskaya sites), the spectra of the food residue contains compounds that were not observed in the pottery matrix and which originate from the food cooked in the pottery vessels. The main question remains: can we obtain a reliable ^{14}C age by dating charcoal from the pottery matrix? The differences between NMR spectra of the food residue and pottery matrix are not significant. In both cases there is the problem of humic acids. During the chemical pretreatment of materials for dating humic acids are removed by alkali-acid solutions. Besides, before dating of charcoal from the pottery matrix humic acids and other admixtures are removed by the treatment of the solution of hydrofluoric aside (Skripkin and Kovaliukh, 1998; Zaytseva *et al*., 2009). Therefore, practically all humic acids are destroyed. Thus, one can assume that we are dating the same materials in both pottery matrix and the food residue. Unfortunately, we did not study the materials dated after chemical pretreatment. It is rather difficult because the fluorine ions used for this are practically impossible to be removed completely and their remains can destroy the glass installations.

It is necessary to note that the additional information concerning the origin of the carbon pottery can be obtained from the delta ^{13}C, but unfortunately we measured this parameter only during AMS dating. The presence in the pottery and the food residue matrix of the unsaturated compounds can testify that the carbon is not of geological origin because these compounds would have been destroyed during the geological time.

This are only preliminary results and we hope that this investigation will be continued in the future.

5. CONCLUSIONS

In recent times, pottery has been used for ^{14}C dating of archaeological events. The first attempt to study the chemical compounds in the pottery matrix and the food residue was carried out using the NMR spectroscopy. Our study has shown that the chemical compounds and chemical bonds in both materials are rather similar.

According to the study one can conclude that chemical compounds can originate from the organic materials used for the pottery forming.

The radiocarbon dates produced from the charcoal of pottery matrix can be reliable if the ooze used was not located deep in a lake and close to the surface of sites.

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