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THE UTILISATION OF THERMAL ANALYSIS TO OPTIMISE RADIOCARBON DATING PROCEDURES

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Abstract

Thermal analysis combined with mass spectrometry was applied to radiocarbon dating procedures (age determination of carbon-containing samples). Experiments carried out under an oxygen atmosphere were used to determine carbon content and combustion range of soil and wood samples. Composition of the shell sample and its decomposition were investigated. The quantification of CO_2 formed by the oxidation of carbon was done by the application of pulse thermal analysis. Experiments carried out under an inert atmosphere determined the combustion range of coal with CuO as an oxygen source. To eliminate a possible source of contamination in the radiocarbon dating procedures the adsorption of CO_2 by CuO was investigated.

Keywords: thermal analysis in radiocarbon dating

Introduction

Radiocarbon dating is one of the main methods used for estimating the age of carbon containing materials. It is based on the measurement of the concentration of the radioactive isotope ^{14}C which occurs in extremely small quantities. ^{14}C is continuously produced by the interaction of cosmic ray neutrons with nitrogen molecules in the atmosphere. The half-life of this isotope is 5600 years. The ^{14}C formed in the atmosphere oxidises to $^{14}CO_2$ and mixes with common $^{12}CO_2$. The ratio of ^{14}C to ^{12}C is in nature constant but when the continuous, dynamic cycle of carbon isotope exchange is stopped (e.g. death) then the amount of ^{14}C slowly reduces by radioactive decay (to ^{14}N) at a rate governed by its half-life. Thus, the age of carbon-containing matter can be determined by measuring its ^{14}C content. Elemental carbon isolated from the sample is the target used in ^{14}C-dating by accelerator mass spectrometry. Thermal analysis was used to investigate the processes necessary for the isolation of elemental carbon.

Experimental

A sample for radiocarbon dating is treated with hydrochloric acid to remove carbon in the form of carbonates, followed by treatment with sodium hydroxide to remove humic acids formed during the rotting process [1]. This procedure should

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leave only the carbon that was incorporated into the organism during its life-time. In order to obtain the carbon dioxide that is later used for the synthesis of elemental carbon a sample is heated in an evacuated sealed quartz tube with CuO as an oxygen source. The quartz tube containing CuO_x is pre-treated in a muffle oven at 900°C for two hours to remove any carbon-containing impurities. The resulting carbon dioxide is mixed with hydrogen in the ratio 2.5:1 and catalytically reduced over cobalt [2] (magnesium [3], iron [4–6]) powder to elemental carbon.

CuO_x was pre-treated by heating at 900°C, left to cool and then analysed under a helium atmosphere on a Netzsch STA 409 thermoanalyzer coupled with a QMG 420 quadrupole mass spectrometer. The temperature was raised at a rate of 10 K min^{-1} over a range of 25 to 1100°C. The amount of CO_2 adsorbed by the CuO during handling was measured using pulse thermal analysis [7]. 1 ml of CO_2 was injected for the quantitative calibration of a m/z=44 mass spectrometric signal. Experiments involving wood, soil and shell were carried out under an oxygen atmosphere at a rate of 10 K min^{-1} in the range 25 to 870°C. The coal sample was analysed under a helium atmosphere using CuO as an oxygen source.

Results and discussion

The CuO_x used as an oxygen source in the radiocarbon dating procedure is produced by the oxidation of copper wires resulting in a product containing CuO and Cu_2O. The determination of the phase composition of this oxide mixture was done by its oxidation (Fig. 1). The result of TG analysis indicates that the product contains 52% CuO and 48% Cu_2O. This phase composition was confirmed by XRD (Fig. 2).

In the first step of the process to obtain elemental carbon a quartz tube containing CuO_x was pre-treated by heating at 900°C in a muffle oven for two hours. The results of thermal analysis of CuO presented in Fig. 3 show that during cooling, CO_2 pres-

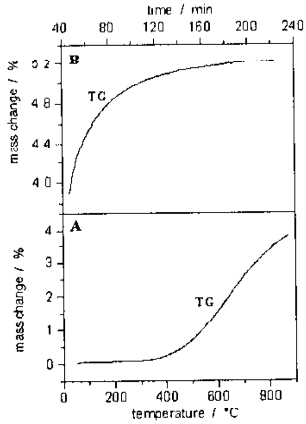

Fig. 1 The oxidation of CuO_x under an atmosphere of 20% oxygen in He. A – heating at a rate of 20 K min^{-1} from 25 to 900°C, B – isothermal heating at 900°C

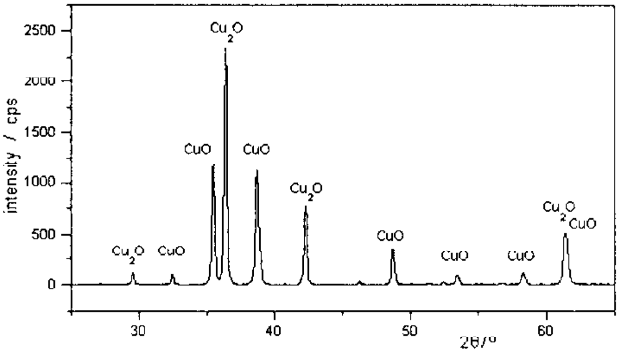

Fig. 2 XRD patterns of CuO_x

t in the atmosphere is adsorbed onto the surface of CuO. This CO_2 (0.4–0.5 wt%)
ntaining so called 'modern carbon' contaminates the sample (increasing the
mount of ^{14}C would decrease the sample age). The evolution of CO_2 from CuO oc-
rs in the temperature range 200–500°C with the a maximum at 315°C. In order to
void errors in the age determination adsorbed 'modern' CO_2 is removed by heating
e CuO in the quartz tube to 500°C under vacuum.

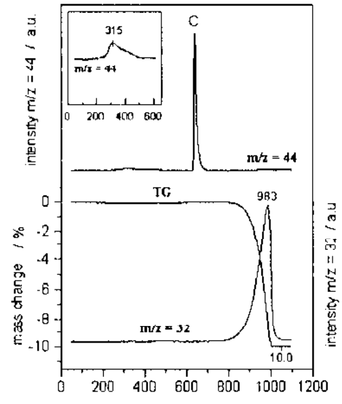

Fig. 3 TA and MS signals resulting from the desorption of CO_2 from CuO before its decomposition 'C' denotes the 1 ml pulse of CO_2 used for the calibration of the *m/z*=44 signal

Thermal analysis was used to determine the temperature range for the evolution
f carbon dioxide formed by the combustion of the coal (Fig. 4). Its reaction with
uO begins at about 300°C. The majority of hydrocarbons present in the coal react
the first stage of oxidation (300–600°C) with a large evolution of water that is su-
rimposed onto the broad peak of CO_2 evolution. The second stage of the reaction

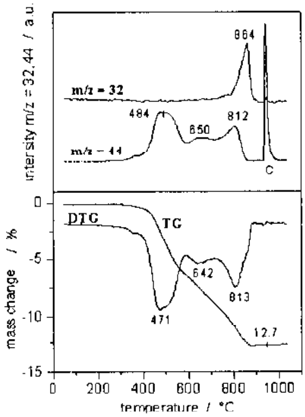

Fig. 4 TA-MS investigation of the combustion of coal in the presence of CuO. 'C' denotes the 1 ml pulse of CO_2 used for the calibration of the *m/z*=44 signal

occurs in the range 580–740°C with the maximum of CO_2 evolution occurring at 650°C. The CuO itself begins to decompose in the third stage of the reaction. The beginning of oxygen evolution due to the reaction:

$$2CuO = Cu_2O + 1/2O_2$$

was determined in a separate experiment and was found to be at about 700°C. The rate of the gas-solid reaction between the oxygen evolved from CuO and carbon, with a maximum of CO_2 evolution at 812°C, is faster than the rate of the solid-solid reaction between CuO and C. Carbon oxidation is finished at about 880°C. The de-

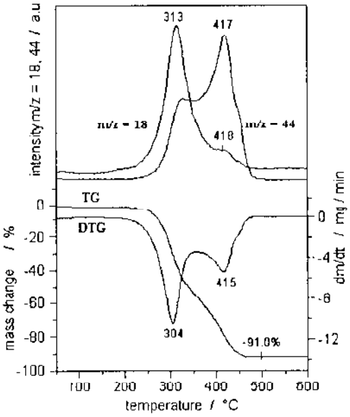

Fig. 5 Combustion of wood in an oxygen atmosphere

composition of any unused CuO is completed at approximately 920°C. The last sharp signal of CO_2 is due to an injection of 1 ml of CO_2 for the quantitative calibration of the mass spectrometric signal *m*/*z*=44.

Three types of sample variety, shell, soil and wood were used in the investigation of radiocarbon dating procedures by thermal analysis. The combustion of wood (Fig. 5) occurs in the range 200–500°C (20% oxygen in He). In the first stage of combustion, water and CO_2 are evolved from the hydrocarbons (cellulose). In the second stage there is mostly carbon left resulting in a main product of CO_2 with the formation of a little water from the residual hydrocarbons. The ash comprises about

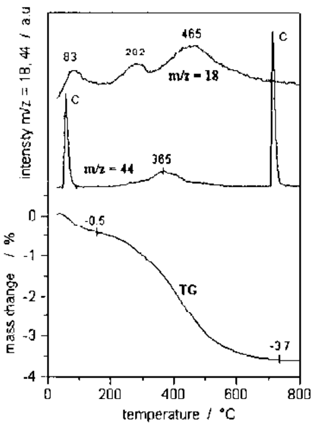

Fig. 6 TA-MS analysis of the soil sample under an oxidising atmosphere. The calibration signals 'C' created by two pulses of CO_2 were used for the quantitative determination of organic carbon

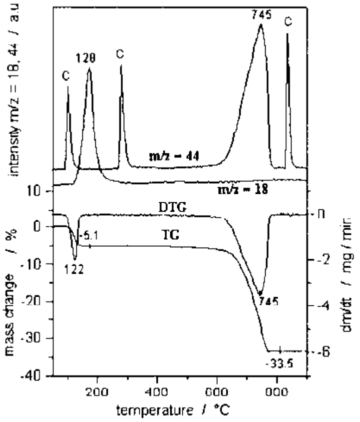

Fig. 7 The evolution of water and CO_2 from the shell sample. The pulses of CO_2 used for calibration of the *m*/*z*=44 signal are marked as 'C'

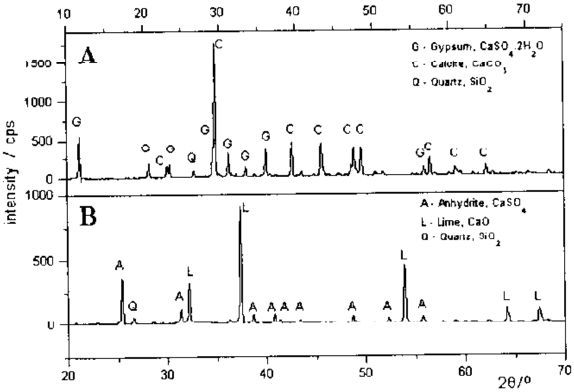

Fig. 8 XRD patterns of the shell sample before (A) and after calcination (B)

9% by weight. In the case of the soil sample (Fig. 6) the organic carbon was determined to be 0.56 wt% and the evolution of carbon dioxide from its combustion occurred in the range 200–700°C with the maximum at 365°C. In the case of the shell sample the evolution of water from the $CaSO_4{\cdot}2H_2O$ occurred in the range 100–300°C and carbonate decomposition took place between 600–790°C (Fig. 7). The XRD data taken before shell decomposition (Fig. 8A) indicate the presence of gypsum, calcium carbonate (calcite) and minor amount of silica (SiO_2). The sample after calcination (Fig. 8B) contains anhydrite ($CaSO_4$), lime (CaO) and silica. Based on these results and using the respective mass losses on the TG curve and the PTA calibrated signal m/z=44, the shell composition was determined to be 63.0 wt% gypsum, 27.8 wt% calcite, 8.4 wt% silica and 0.8 wt% of organic matter.

Conclusions

Thermal analysis applied to radiocarbon dating processes gives much information which can be used for optimising elemental carbon synthesis. The TA experiments carried out under oxygen enabled the quantitative determination of carbon present in the investigated samples. The exact determination of the carbon is possible from the analysis of the mass spectrometric signal of evolved CO_2 using PTA calibration. This, in turn, allows for the preparation of the optimal amount of sample while still giving a sufficient amount of elemental carbon for ^{14}C-dating. The application of TA performed under an inert atmosphere enabled the investigation of the reaction ranges of carbon-containing samples with CuO as an oxygen source. PTA with its ability to quantitatively analyse tiny amounts of carbon proved that the radiocarbon process intended to remove carbon-containing impurities (ampoule pretreatment at 900°C) actually introduces adsorbed CO_2. An investigation of the desorption process by TA has shown how to avoid this source of secondary contamination.

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