Bulletin de la Société belge de Géologie	T. 94	fasc. 2	pp. 113-115	Bruxelles 1985
Bulletin van de Belgische Vereniging voor Geologie	V. 94	deel 2	blz. 113-115	Brussel 1985

AN ACCURATE ZINC CHARCOAL REDUCTION SYSTEM FOR D/H MEASUREMENTS OF WATER AND CELLULOSE

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ABSTRACT. - An improved method for reducing water and cellulose nitrate to hydrogen gas for deuterium determination, applicable to paleoclimatic studies, is described, using zinc and charcoal.

Keywords : - deuterium
- cellulose nitrate
- zinc
- reduction (chemistry)
- paleoclimatology.

INTRODUCTION.

The application of deuterium isotope measurements in fossil wood and peat deposits is of increasing interest in the field of paleoclimatology.

This paper deals with the technical aspects of the procedure. For the climatic interpretation of the results is refered to a former publication (A. D. DUBOIS, 1984-1).

In order to be suitable for measurement of the D/H ratio by a light-element mass spectrometer, a water sample has to be reduced to hydrogen gas quantitatively. In the case of cellulose, water is produced by total combustion.

The measured isotopic ratio is expressed relative to the international V-SMOW water standard. Thus, in the case of cellulose analysis, water samples have to be reduced regularly to calibrate the system.

Although uranium can be used successfully as a water reducing agent (J. BIGELEISEN *et al.*, 1952; S. EPSTEIN *et al.*, 1976), previously described reduction systems using zinc (W.E. SCHIEGL and J. C. VOGEL, 1970; G. L. LYON and M. A. COX, 1980) show several disadvantages. However, the use of zinc instead of uranium has the distinct advantage of being inexpensive, safe and easily available in all countries.

Moreover, zinc unlike uranium doesn't produce a fine dust along the preparation system, which may cause problems of memory effects and contamination of previous samples.

The present article, which deals with an alternative method to the sealed zinc tube technique published by M. L. COLEMAN *et al.* (1982), describes a zinc reduction system for water and cellulose with the following features :

1. Simplicity of construction; no circulation or Toepler pump is required, hence the fractionation and contamination of the hydrogen gas is minimised.
2. No corrections need to be applied for consecutive samples.
3. Water samples as small as 5 µl are successfully reduced.
4. One zinc filling is good for at least 70 reductions of ca. 5 µl water samples.
5. An efficient combustion system for cellulose nitrate is on-line with the zinc reduction tube.
6. Cellulose nitrate combustion is completed in less than 10 minutes.

EXPERIMENTAL SECTION.

APPARATUS. The apparatus consists of a 9 mm diameter pyrex preparation line (fig. 1) of which the principal components are a sample introduction system, consisting of

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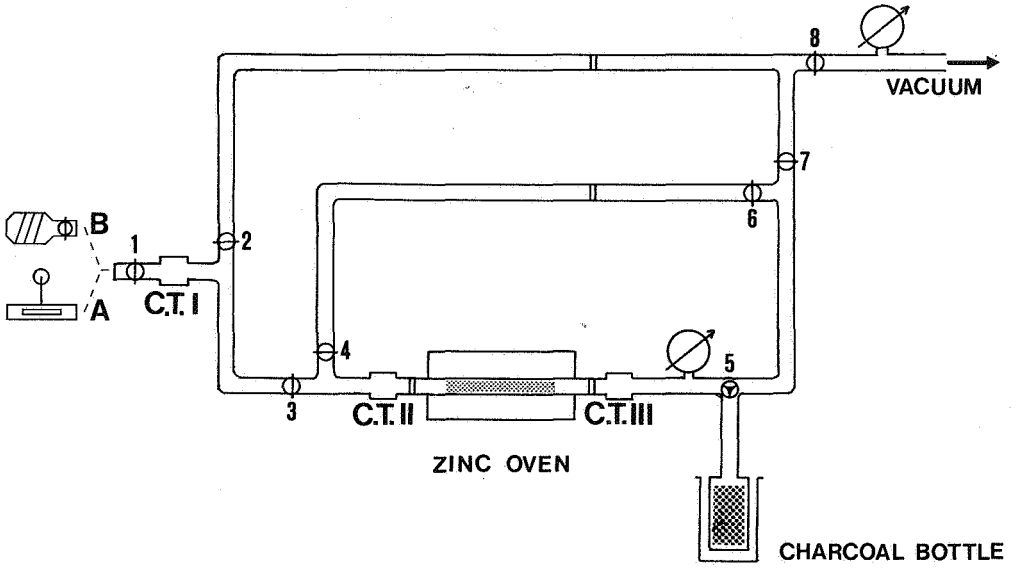

Fig. 1 - The reduction system : A. water sample cracking device;
B. cellulose nitrate combustion bottle;
C. T. cold trap.
The taps are numbered from 1 till 8.

a capillary system for water or a cellulose nitrate sample bottle, a zinc tube heated in a tube furnace and an adsorption bottle containing activated charcoal. The whole system is evacuated by means of a common rotary pump which backs the 2001/s-1 oil diffusion pump with associated foreline trap. The vacuum taps, slightly greased with silicon-based vacuum grease, are of the fluorocarbon o-ring type. The system can be automated with pneumatically operated high-vacuum glass taps (C.A.M. BRENNINKMEIJER, 1981). PIRANI and PENNING gauges are included for vacuum monitoring. The furnace temperature is regulated by a thermocouple at the centre of the furnace.

REAGENTS. The reducing agent consists of 30 g of 425-800 μm granulated zinc, retained in a pyrex tube by means of glass wool and stainless steel gauze with a pore size of 42 μm.
The zinc is constantly heated at $\pm$ 380° C.
15 g of activated charcoal, 0.3-0.5 mm in diameter, cooled with liquid nitrogen, is used as adsorbent of the hydrogen. This charcoal has been completely outgassed at 300°C prior to use.

PRODECURE.

A. WATER ANALYSIS.

A capillary tube of about 0.5 mm internal diameter containing no more than 5 μl water is sealed in a flame and placed in a sample cracking device. After evacuation of air across taps T.2 en T.8 the capillary is broken and the water frozen out in cold trap C.T. I, cooled with liquid nitrogen and the non-condensable gases eliminated.

Cold trap I is warmed up whilst taps T.2 and T.4 are closed and the water transferred to cold trap II by means of pumping via taps T.3, T.5, T.7 and T.8. Afterwards tap T.3 is closed. The ice is vapourized at room temperature and drawn through the granulated zinc at $\pm$ 380°C, and the evolved hydrogen gas adsorbed onto the cooled charcoal by monitoring the two-way stopcock T.5. The initial pressure rise and subsequent pressure fall due to adsorption can be followed on the Pirani gauge.

Any remaining water in cold trap III is returned over the hot zinc by changing the two-way stopcock T.5, with cold trap III at room temperature and cold trap II at liquid nitrogen temperature, whilst taps T.4 and T.6 are open and T.7 is closed. Two passages of approx. ten minutes ensure complete conversion of a 5 μl water sample.

The charcoal bottle is removed and the D/H content measured directly by means of a double collector mass spectrometer (V.G. 602D).

After evacuation of the preparation system up to a pressure of 10^{-3} mbar, the next sample can be prepared.

B. CELLULOSE ANALYSIS.

The system can be easily altered to measure the deuterium content of cellulose, an assay with applications in e.g. paleoclimatology, hydrology (A.D. DUBOIS, 1984-2) and food analysis.

Prior to combustion, the cellulose is nitrated to remove the exchangeable hydroxyl groups.

The combustion is performed by heating ca. 40 mg cellulose nitrate to $\pm$ 350°C together with 1g granular CuO and 700 mg copper turnings $\pm$ 0.1 mm thick, in an evacuated pyrex bottle of about 50 ml on-line with the system (fig. 1).

After total combustion i.e. ± 10 min, the resulting water is trapped in cold trap I cooled at ca. -80°C, eliminating non-condensable gases such as CO_2. The water is further reduced as mentioned above. After use the combustion bottles are thoroughly cleaned with a H_2SO_4-$K_2Cr_2O_7$ mixture.

RESULTS AND DISCUSSION.

To test the reproducibility of the preparation technique, the international V-SMOW water standard has been reduced and measured 40 times between routine samples, yielding a δ value of 43.4 °/₀₀ (relative to our working standard) with a standard deviation of + 0.8 °/₀₀ .

Unlike previous zinc systems one zinc filling is good for at least eighty reductions without correction.

Moreover, replacement of the zinc does not affect the results obtained. The memory effect of the system is ± 0.5 ‰. To test wether the reduction system caused any systematic errors, the international SLAP and GISP water standards were measured againgst V-SMOW (R. GONFIANTINI, 1984).

δD(SLAP) = - 427.8 °/₀₀ compared with the recommended value of - 428 °/₀₀

δD(GISP) = - 191.2 °/₀₀

δD(GISP) normalised = - 191.3 °/₀₀ .

The average analytical precision of the D/H assay on cellulose nitrate samples is ± 2 °/₀₀ .

ACKNOWLEDGMENT.

The author thanks R. VANHOORNE, D. K. FERGUSON, H. DESSEYN, B. VAN DER VEKEN, E. VANSANT and G. PEETERS of the University of Antwerp, P. TRIMBORN and W. STICHLER of the Institut für Radiometrie, NEUHERBERG, F. R. G. and C. A. M. BRENNINKMEIJER of the Institute of Nuclear Sciences, New Zealand for helpfull discussions, advice and encouragements. The assistance of A. TORFS in preparing the samples is also acknowledged.

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Manuscript received on october 1984.