

## An automated method for the analysis of 'particulate' carbon and nitrogen in natural waters

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### Abstract

A method is described for the measurement of the carbon and nitrogen content of particulate material in natural waters. Particulate material is separated by filtration through GF/C filters. The dried filter is encapsulated in silver foil using a purpose made press. Analysis is carried out using high temperature combustion with thermal conductivity detection of emission gasses. Analytical performance characteristics obtained with both standards and natural materials are given.

### Introduction

Carbon and nitrogen are two of the principal elements of organic matter. A knowledge of their particulate concentrations and ratios in plankton samples is useful when assessing the productivity of natural waters. Sharp (1974) described a method for determining particulate carbon and nitrogen in sea water using glass fibre filters and gas chromatographic separation of the gaseous products after high temperature combustion in a manually operated instrument. More recently, automated instruments have become available, but they require the sample to be physically small, a problem when samples are contained on glass fibre filters. Hauser (1973) described a method which involved major modifications to the instrument and Downs and Lorenzen (1985) overcame the problem by using small silver filters. Here we describe a method which is simple and rapid but utilizes the more conventional glass fibre filters which are inexpensive and readily available.

### Method

An Erba Science 1106 Elemental analyser equipped with a DP110 integrator was used. Sam-

ples were combusted at about 1000°C in the presence of oxygen and a catalyst. The combustion gasses were separated by gas liquid chromatography and the integrals of the peaks obtained from a thermal conductivity detector, at the outlet of the GLC column, were proportional to the quantity of the C, N and H present in the sample. All the instrumental conditions i.e. reagents, gas pressures, flows etc, were as recommended by the manufacturer except for:

i) An industrial grade argon-free, oxygen (BOC special gasses) was used instead of ultra-pure oxygen. The nitrogen blank of the gas alone was still negligible but the reagent costs were considerably reduced.

ii) In early work the combustion reactor packing was, from the bottom up: 5 mm quartz wool; 45 mm silvered cobaltous-cobaltic oxide; 5 mm quartz wool; 110 mm chromium oxide; 5 mm quartz wool. However, in later work an alternative packing was used (viz. 5 mm quartz wool; 15 mm silver wool; 5 mm quartz wool; 75 mm copper oxide; 5 mm quartz; 60 mm chromium oxide; 5 mm quartz wool) which gave calibration (k) factors and analytical statistics which were the same as the original packing but was both considerably cheaper and more readily available.

15-mm diameter filter discs were cut from larger diameter GF/F filters using a cork borer. All filters were ashed at 550°C for several hours; the ashed filters were stored in clean glass jars until required. Samples were prepared by passing sufficient water samples through a miniature filter holder turned from two pieces of teflon, so that at least 5 µg of carbon was retained in the filter. The filters were dried for 5 minutes at 80°C then stored in a desiccator in the dark. Dried filters were folded and placed in the corner of a square of 0.04 mm thick tin foil ('Tin foil pieces for phosphate reagent', B.D.H. Chemicals) of approximately 1 cm side. (Fig. 1). The foil and filter were then rolled as tightly as possible using two pairs of forceps, starting from the corner containing the filters and rolling diagonally. The ends of the roll were folded over to produce a cylindrical package < 15 mm long and less than 3 mm diameter. The sample was then introduced into the press (Fig. 2) and pelleted by applying pressure to the two ends. The pelleted sample was removed by means of a clean metal rod.

### Results and discussions

The instrument was originally calibrated by placing different weighed quantities of the standard, acetanilide, directly into tin capsules and also onto glass fibre filters which were prepared for analysis as described above. After correction for the appropriate blanks, integral values obtained by both procedures lay on identical lines for each element. For routine use tin capsule standards were analysed in order to reduce the build up of glass-fibre residues on the column. Carbon and nitrogen calibrations were linear to at least 400 µg C and 60 µg N. A single calibration for C and N was

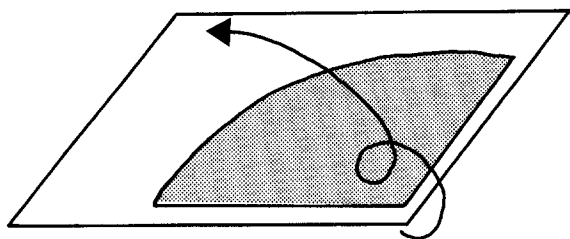


Fig. 1. The location of the folded filter paper on the tin foil at the start of the rolling procedure and the direction of rolling.

found to be applicable over several weeks, although it was checked several times in each analytical run using weighed standards in tin capsules. Both calibration lines had small negative intercepts on the integral axis and sensitivities of 810 and 2243 integral counts/µg, N or C respectively were obtained. Limits of detection for particulate carbon

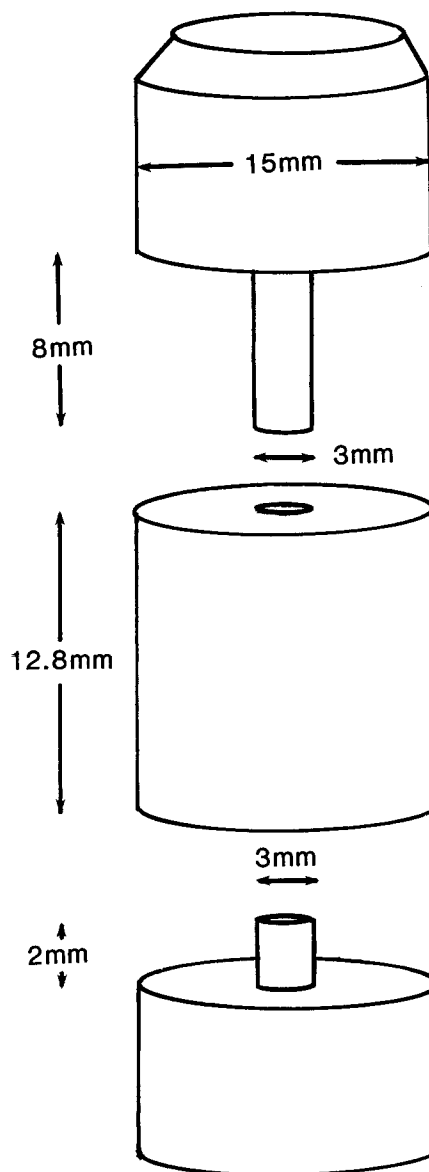


Fig. 2. The capsule press. The press was turned in brass with the pushthrough rod (not shown) made from 3 mm diameter stainless steel rod; it is important that the compression ends of the press in contact with the sample are machined flat as shown.

and nitrogen were 2.1  $\mu\text{g}$  and 3.7  $\mu\text{g}$ , respectively, using the definition of Wilson (1973, 1974) i.e.  $LD = 2\sqrt{2} t \cdot SD_B$ , where  $t$  is the single-sided student's  $t$  value at 95% confidence limit and  $SD_B$  is the standard deviation of a series of blank analyses. The precision of natural samples was determined by filtering 10 replicates (100 ml) of a homogeneous sample of water from Windermere. These gave means and standard deviations respectively of 14.37  $\mu\text{g}$  and 0.307  $\mu\text{g}$  for N and 80.59  $\mu\text{g}$  and 3.009  $\mu\text{g}$  for C, i.e. relative standard deviations of 2.1% for N and 3.7 for C.

The Erba Science 1106 is designed to work automatically with a top mounted carousel feeding samples by gravity, via an air lock, into the combustion chamber. The residue from normal samples (i.e. not on glass fibre filters) is caught in either a small quartz or nickel crucible. However, the size of the compressed glassfibre filter residues caused them to adhere frequently to the top of the crucible, stopping later samples from reaching the hottest part of the furnace and producing incomplete combustion. The only practical remedy was to discard the crucibles and allow the residues to build up on the top layer of quartz wool. The residues were removed subsequently from a disconnected cold tube using quarter inch (6 mm) high speed drill bit, braised onto a long steel shaft and rotated by hand while applying slight pressure. With time this method powders the surface chromium oxide which reduces the gas flows. The small layer of powdered

$\text{CrO}_2$  was be removed and the original volume made up with new material. The chemical packings of the columns required changing at the rate recommended by the manufacturer; however, the large size of the filter residue reduced the number of analyses which could be carried out before the tube became blocked. Tests showed that if more than 20–25 filter samples plus a few normal standards (not on filter discs) were analysed, recoveries, particularly of nitrogen, were reduced considerably. In routine operation, two combustion tubes were kept packed and used alternately, one in the instrument whilst the other was disconnected for removal of the filter disc residues. In this mode, two batches could be run in a 24-h period (i.e. 40–50 samples), one batch being run overnight.

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