

# A fast method to prepare water samples for $^{15}\text{N}$ analysis

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**Abstract** Automatic element analyser is often used to prepare organic matters for  $^{15}\text{N}$  analysis. It is seldom used to prepare water samples. Water samples are conventionally dealt with by Kjeldahl-Rittenberg technique. But it requires tedious and labor-intensive sample preparation. A fast and reliable method is proposed in this paper to prepare water samples for  $^{15}\text{N}$  analysis.

**Keywords:** water samples, N analysis, fast preparation.

## 1 Introduction

Nitrogen cycle is one of the most important element cycles in the hydrosphere and is probably the one most influenced by human activity. Present industrial fixation of  $\text{N}_2$  into nitrogenous fertilizers, together with modern farming practices and effluents from industrial and domestic sources, may result in the contamination of groundwater and surface water by nitrate. Nitrogen stable isotope plays a key role in tracing the sources and causes of nitrogen pollution in the hydrosphere<sup>[1–3]</sup>. Fast and reliable methods to prepare water samples for  $^{15}\text{N}$  analysis are essential for extensive use of nitrogen stable isotopes.

Preparation of water samples for N stable isotope analysis is traditionally achieved by Kjeldahl steam distillation and Rittenberg techniques<sup>[2]</sup>. This process requires skilled operation of specialized equipment as well as considerable processing time and causes cross contamination between samples. The main alternative to Kjeldahl – Rittenberg technique is Dumas combustion<sup>[4]</sup>. It has many advantages over the Kjeldahl – Rittenberg technique. However, Dumas combustion apparatus that has been used for nitrogen isotope analysis is so sophisticated that it is not easy to establish one for most laboratories. Use of less sophisticated apparatus may lead to inaccuracies in nitrogen isotope analysis owing to the presence of small amounts of carbon monoxide, hydrocarbons at  $m/z$  28 and  $m/z$  29 and nitrogen oxides at  $m/z$  30. We attempt to solve this problem by the use of automatic elemental analyzer (EA) after separation and enrichment of water samples with ion exchange chromatography and diffusion method.

## 2 Analytical procedure

The ammonia and the nitrate ions in water samples can be quantitatively isolated with the use of ion exchange resins without being exposed to the atmosphere after the water samples are filtered through filter paper<sup>[5]</sup>. These ions are eluted from ion exchange resins by saturated  $\text{K}_2\text{SO}_4$  or

KCl solution. The eluants are made basic after being poisoned with  $\text{HgCl}_2$  in disposable plastic specimen containers to volatilize  $\text{NH}_4$  into acid-washed zeolite in tin combustion cups (Nitrate-bearing eluants need addition of Devarda's ally)<sup>[6]</sup>. Zeolite samples are then combusted on an elemental analyzer to oxidize  $\text{NH}_4$  to  $\text{N}_2$ .

The elemental analyser should be equipped with an oxygen loop and an auto-sampler. A batch of samples is introduced sequentially into the elemental analyzer by the autosample. The carrier gas is highly pure helium (99.9995%). In the analyser, the sample undergoes flash combustion with pure oxygen (99.998%) in a quartz tube (combustion tube) with chromium oxide, copper oxide and silver wool. The products then automatically transfer to another quartz tube (reduction tube) with the carrier gas, in which the products such as nitrogen oxides are reduced and excess oxygen is removed on hot copper. Magnesium perchlorate in a glass tube is used as water trap.  $\text{N}_2$  and  $\text{CO}$  were separated in a gas chromatograph column (GC) before gas is introduced to the mass spectrometer. If the elemental analyser is equipped with a thermal conductivity detector (TCD), it is possible to simultaneously determine total N in samples. The operating conditions of elemental analyser are shown in Table 1.

Table 1 Typical operating conditions

Operation	Conditions
Combustion tube	1020°C
Reduction tube	600—650°C
GC	30—50°C
TCD	90°C
Sample drop	30 seconds after start of $\text{O}_2$ pulse
He carrier flow	60—80 $\text{mL} \cdot \text{min}^{-1}$
Oxygen pulse length	25 seconds

Continuous or batch methods can be used to interface the elemental analyser with mass spectrometer<sup>[7]</sup>. Batch methods enable more precise isotope ratio analysis but require sample trapping; continuous interfaces are simpler and do not interrupt GC operation.

### 3 Discussion and conclusions

Studies have been carried out to test for fractionation effects during the separation and enrichment of  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N and the conversion to  $\text{N}_2$ .

Garten<sup>[5]</sup> used Dowex 50W-X8 and 1-X8 to collect ammonia and nitrate, respectively. His quality assurance tests showed that adsorption efficiency of ammonia and nitrate was more than 95% and more than 97%. Recovery of ammonia and nitrate by ion exchange through the elution step was  $\approx 100\%$ . No significant fractionation effects were introduced during ion exchange. But high concentrations of anions in water samples can interfere with nitrate adsorption on the anion exchange resins (Bio-Rad<sup>3</sup> AG1-X8), which may result in isotope fractionation of nitrogen. Chloride, sulfate, and potassium biphthalate, added to  $\text{KNO}_3$  standard solutions caused no significant nitrogen fractionation for chloride concentrations below about 200 mg/L in 1000 mL samples, sulfate concentrations up to 2000 mg/L in 100ml samples, and potassium biphthalate concentra-

tions up to 200 mg/L in 100ml samples. It indicates that in most cases these resins used are effective<sup>[8]</sup>.

The test for ammonia and nitrate trapping efficiency indicated that a minimum of 97% of ammonia and nitrate in samples were reliably collected by zeolite traps<sup>[6]</sup>. No significant fraction of nitrogen isotope occurred during this procedure. Water samples should be poisoned by  $\text{HgCl}_2$  to restrict microbe activity before diffusion. Although it takes more time to prepare water samples by diffusion method than by Kjeldahl steam distillation, it is considerably faster since large numbers of water samples can be prepared during a single incubation.

In conventional nitrogen isotope analysis, the excess of sample servers to facilitate handling and reduce leakage problems in vacuum system, and to maintain viscous flow conditions and constant pressure in the MS inlet. Because samples are always accompanied by a large pressure of carrier gas, it is possible to maintain the viscous flow conditions at a low sample pressure used. The range of sample sizes may thus be varied considerably. Continuous methods theoretically allow precise analysis of as little as 10-100 nmol of  $\text{N}_2$ <sup>[7]</sup>. Furthermore, memory effects can be reduced as element analyser is continually swept with carrier gas. However, a non-linear effect of the element mass in the sample on the results from an EA-MS measurement is often observed. It can be solved by the use of calibration model<sup>[9]</sup>. The model corrects for both drift and non-linearity, and thus allows a wider range of sample masses in the batch.

The above method is especially suitable for the preparation of large numbers of water samples for  $^{15}\text{N}$  analysis. The usual operation is: (1) separation of ammonia and nitrate in the field with ion exchange chromatography; (2) Diffusion of eluants in a laboratory; (3) Oxidation of  $\text{NH}_4$  to  $\text{N}_2$  on automated element analyser.

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