

Simultaneous Determination of Ar/N₂ Ratios in Groundwater

지하수에 용해된 질소, 아르곤 가스의 동시측정

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Abstract: Previously reported Ar/N₂ ratios in groundwater have been measured by single ion monitoring (Barnes *et al.*, 1975; Vogel *et al.*, 1981; Mariotti *et al.*, 1988). The detector geometry and flared flight tube in VG Optima isotopic ratio mass spectrometer appeared to be fortuitously aligned for the simultaneous measurement of Ar/N₂ ratios. Method development included mechanical adjustments to optimize the mass spectrometer for Ar/N₂ ratio measurements followed by development of a preparation system for the extraction of air-saturated water samples. Samples containing known Ar/N₂ ratios were used to assess accuracy and precision, and to test the applicability of methods for measurements of aqueous Ar/N₂ ratios. The results indicated that the prepared air-saturated water samples were almost identical to the predicted Ar/N₂ ratios ($p < 0.001$). Groundwater samples were collected from on-going research sites, Shelton and Grand Island, Nebraska. Samples from the Grand Island sludge injection site form a lower boundary for worldwide reported Ar/N₂ ratios. These lower Ar/N₂ ratios can be explained by the production of nitrogen gas from this site, where denitrification was reported previously.

요약: 지하수의 Ar/N₂가스의 비율은 탈질화(denitrification)의 정도를 측정하는 하나의 방법으로 사용된다. (Barnes *et al.*, 1975; Vogel *et al.*, 1981; Mariotti *et al.*, 1988) 그 비율 측정은 일반적으로 질량분석기(Mass Spectrometer)를 사용한다. 본 실험에서 사용한 Mass Spectrometer는 일반적인 Static Mass Spectrometer가 아닌 Ar과 N₂을 시간적으로 동시에 측정하여 오차를 줄일 수 있는 VG Optima isotope ratio Mass Spectrometer를 사용하였다. 두 지역 지하수의 Ar/N₂가스의 비율을 측정한 결과 Site 1(Grand Island, NE)의 경우 대기가스가 포화된 증류수의 Ar/N₂가스 비율인 0.026보다 낮은 0.015-0.018로서 탈질이 일어났음을 알 수 있으며; Site 2(Shelton, NE)의 경우 0.023-0.027로서 탈질이 일어나지 않음을 알 수 있다. 본 실험의 목적은 지하수에 용해되어 있는 Ar/Nitrogen의 비율을 정확히 측정하는 방법을 개발하므로써 탈질의 정도를 정확히 측정하며 탈질의 전개 과정을 관찰하기 위한 것이다.

INTRODUCTION

Since argon has a higher aqueous solubility than nitrogen, the atmospheric Ar/N₂ ratio of 0.012 is lower than that in air-saturated water. Solubilities of Ar and N₂ at saturation with respect to atmospheric levels was expressed as a function of temperature and salinity in Weiss(1970). The degree of nitrogen saturation can be estimated by the ratio of nitrogen to a noble gas-usually argon. Ar/N₂ ratios lower than those predicted at atmospheric saturation are generally considered to result from N₂ excess or entrapment of air. In pore water and groundwater of marine sediments, excess dissolved N₂

has been used as an indicator of microbial induced denitrification (Barnes *et al.*, 1975; Vogel *et al.*, 1981). In groundwater flow systems, these ratios have been used to indicate relative residence times (Almon and Margaritz, 1990) and to indicate whether recharge occurred under differing conditions (Heaton, 1981).

The objective of this research is to develop a method of simultaneous measurement of Ar/N₂ ratios and to apply the method to groundwater samples. Thus the research attempts to provide both improved analytical and aqueous extraction procedures. The so-called "peak jumping procedure" in isotope ratio mass spectrometer has been mentioned in several reports(Vogel *et al.*, 1981; Almon and Margaritz, 1990). In this procedure, the beam is usually first focused on the major ion and counted. Then the second beam is manually focused on the minor ion collector by rearranging the electromagnet. Static mass spectrometer measurements of Ar/N₂ are also

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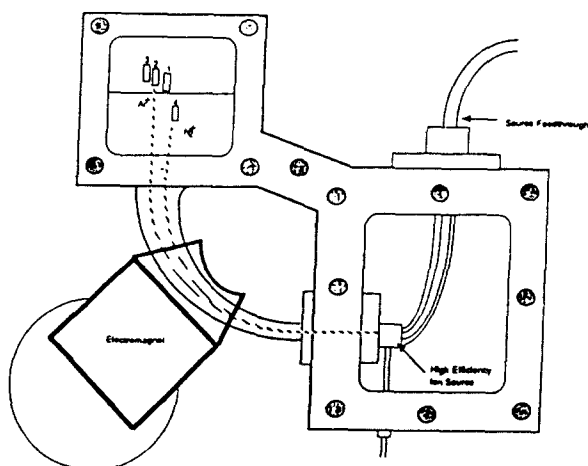


Figure 1. Geometric configuration of optima flight tube and collectors.

commonly reported (Vogel *et al.*, 1981; Almon and Margariz, 1990) which rely on a single collector that requires refocusing for each ion of interest. The obvious disadvantage in either of these techniques is that both procedures rely on the separate collection of the two individual ion beams ($m/q=28$ or 40). Because of the inherent increase in precision, a method to measure Ar/N₂ simultaneously and precisely would have immediate applicability in monitoring denitrification in several on-going groundwater projects.

METHODS

In many cases, mass spectrometer is used to measure isotopic ratios which is one or two mass differences. However, measurements of large different masses, such as mass 40 argon, and mass 28 nitrogen, are required the special geometry of collector in order to measure these mass differences simultaneously for maximization of precision. Beam focusing calculation indicated that existing geometry of the collectors combined with the unique flared flight tube in the VG Optima isotope ratio mass spectrometer (Fisons Instruments, VG Iso-tech, Aston Way, Middlewich, Cheshire, UK) allowed proper alignment for the simultaneous measurement of Ar⁺ and N₂⁺.

Figure 1 shows the plan view of source and collectors. The flared flight tube allows collection of mass 28 in cup 4 and mass 40 in cup 2 after passage through the full magnetic field. Gases are positively ionized in the source and their ion beams are accelerated by a present acceleration voltage. The beams are deflected in the magnetic sector of the flight tube and detected in the collector cups. The amount of deflection can be calculated by the equation:

$$M/Z = B^2 r^2 / 2V \quad (1)$$

where M =ion mass in amu, Z =ion charge (equal to +1), B =uniform magnetic field strength in gauss, r =radius of curvature of ion beam in cm, and V =ion acceleration in volts. Following rearrangement and setting $Z = +1$

$$r = (2MV)^{1/2} / B \quad (2)$$

Calculation indicates that the radius of curvature of the ion beams in the flared tube after passage through the full magnetic field would allow for collection of mass 40 in cup 2 and mass 28 in cup 4. The relative radii of two curvatures can be calculated by assigning $(2MV)^{1/2} / B$ to random magnetic field strength (B) is assumed to be constant;

$$r_{\text{cup2}} = (2 \times 40 \times 3141.5)^{1/2} / B = 501.3 / B$$

$$r_{\text{cup4}} = (2 \times 28 \times 3141.5)^{1/2} / B = 419.4 / B$$

$$\text{SO, } r_{\text{cup2}} / r_{\text{cup4}} = 501.3 / 419.4 = 1.1952$$

The radius of curvature for mass 40 (Ar) in cup 2 is 1.1952 times larger than the radius for mass 28 (N₂) in cup 4. This difference of radii of two curvatures allows proper alignment for the simultaneous measurement of Ar/N₂ ratios.

Preparation of Air-Saturated Water

Air-saturated water samples were prepared by bubbling air through a glass frit into tap water for one hour (Weiss, 1970). An air pump was employed to aerate the water (temp = 20 °C) at a rate of 25.4 cm³/min for one hour. Immediately after saturation 100 ml aliquots of water were removed using glass gas-tight syringes.

Preparation Line for Gas Purification

Water samples were purged of gases and the gas samples were purified for mass spectrometer analysis by a modification of procedure of Benson and Parker (1961)

A 100 ml gas-tight syringe was mounted with a luer-loc onto a round, one liter flask. The syringe was tipped on an angle to prevent trapping of air bubbles between the fittings. Observed air bubbles between the syringe and the water flask were displaced and eliminated deionized water. Under vacuum, the water sample in the gas tight syringe is rapidly drawn into the sputnik which is mounted on the preparation line. As the water sample boils under vacuum in the flask, gas is transferred into the evacuated preparation line. In the line the ethanol/dry ice trap (-78 °C) cryogenically removes water vapor. The evolved gas was cycled through two liquid nitrogen cold traps and a copper furnace (400 °C), purifying the N₂ and Ar of O₂, CO₂ and other gaseous oxides. CO₂ was removed by cycling through a CuO furnace at 700 °C. After cycling for one hour, first through a copper oxide furnace,

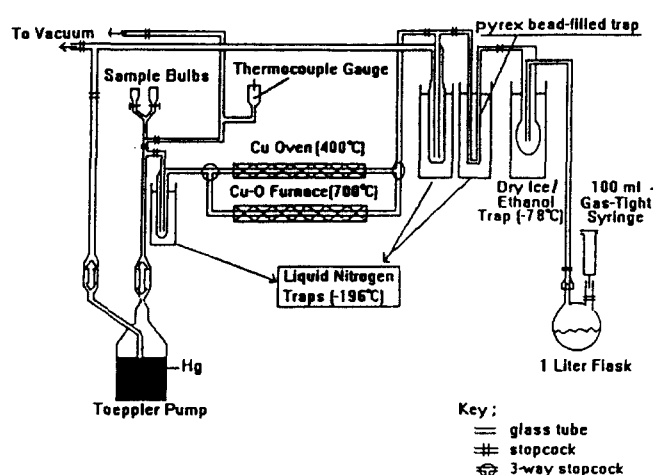


Figure 2. Diagram of preparation line.

then through a copper oven, The purified Ar and N₂ is transferred to a sample bulb by means of a toepler pump. Mass spectrometer scans indicated the purified gas to be free of H₂O_(v), O₂ and CO₂.

Sample Collection

Groundwater samples were collected from multilevel samplers beneath two research sites in the Platte Valley region of Nebraska. The sites were chosen on the premise that the groundwater beneath the Grand Island site is reducing and denitrification has been isotopically confirmed (Spalding *et al.*, 1993) while the groundwater at Shelton is oxidizing and not capable of supporting denitrification.

Preventing atmospheric contamination during sample collection is important. Groundwater samples for Ar/N₂ ratio measurements were collected from flow through cells with 100 ml of gas tight syringes. A Tconnector containing a septum was connected between the well head and peristaltic pump. After sufficient water had been purged through pumping to ensure the representativeness of samples the gas tight syringe was injected into the septum to collect the flowing water.

RESULT AND DISCUSSION

Following the conventional expressing of stable isotopic ratios of other gases, Ar/N₂ ratio is expressed as delta(δ). The Ar/N₂ ratio in a sample being compared to the Ar/N₂ ratio in a standard is expressed in parts per thousand (permil) as follows;

$$\delta^{40}\text{Ar} = \left\{ \left(\frac{\text{Ar}/\text{N}_2(\text{sample})}{\text{Ar}/\text{N}_2(\text{standard})} - 1 \right) \right\} \times 1000. \quad (3)$$

The reference standard, sometimes referred to as the working standard, is air.

Table 1. Ar/N₂ ratios of prepared waters

Sample No.	Ar/N ₂ Ratio	Delta
1	0.0260	1170
2	0.0260	1171
3	0.0259	1164
4	0.0258	1160
5	0.0269	1168
6	0.0260	1170
Standard	0.0001	3.8
Mean	0.0259 ± 0.0001	1167 ± 4

*Atmospheric standard Ar/N₂ ratio: 0.934‰=0.01196, Expected Ar/N₂ ratio of prepared waters at 24°C: 0.0260.

Table 2. Ar/N₂ ratios of groundwaters from Site 1 (Grand Island, NE).

Sample	Ar/N ₂ ratio	Delta
ML-7.5-2 ^a	0.0176	471
ML-7.5-2	0.0175	463
ML-15-1	0.0179	497
ML-15-2	0.0180	505
ML-18-1	0.0148	241
ML-18-2	0.0149	244
ML-19.5-1	0.0158	321
ML-19.5-2	0.0161	345
ML-21-1	0.0157	314

^aSample is from 7.5 meter below ground at multi-level well and samples were duplicated from each depth.

Air-saturated water samples containing known Ar/N₂ ratios were used to assess accuracy and precision. The laboratory results of prepared waters that were extracted and prepared for Isotopic Ratio Mass Spectrometer (IRMS) analysis are shown in Table 1.

Based on the solubilities of nitrogen and argon in groundwater, the expected Ar/N₂ ratio of air-saturated water samples at 24°C was 0.02599. The difference of Ar/N₂ ratios between the prepared samples and the expected ratio was not significant ($p < 0.001$).

Groundwater was collected from two on-going research sites. The sites were chosen to demonstrate waters where differences in ratios were expected to be large. Groundwater beneath the Grand Island sludge injection site (Site 1) was previously shown to be denitrifying (Spalding *et al.*, 1993) while that at the Shelton site (Site 2) is oxidizing and contains equivalent level of nitrate with depth throughout the primary aquifer. Nitrogen gas concentration in Site 1 plotted on Figure 3 suggests that there were higher amounts of N₂ than

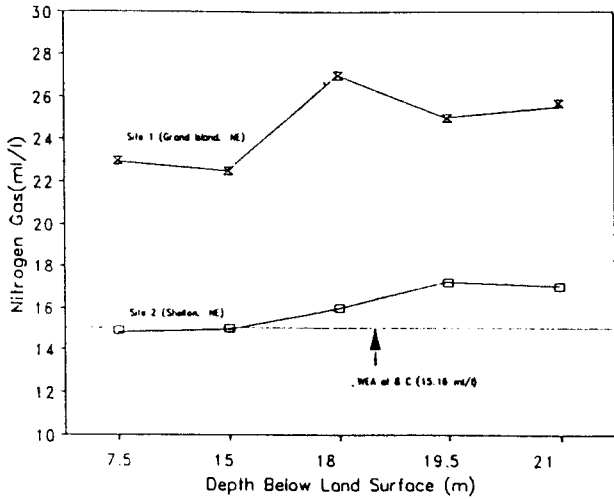


Figure 3. Nitrogen gas concentration at each depth in the Site 1 and Site 2.

Table 3. Ar/N₂ ratios of groundwaters from Site 2(Shelton,NE).

Sample	Ar/N ₂ ratio	Delta
*ML-4.5-1	0.0272	1278
ML-4.5-2	0.0277	1317
ML-6-1	0.0270	1257
ML-6-2	0.0270	1257
ML-7.8-1	0.0249	1079
ML-7.8-2	0.0251	1100
ML-12-1	0.0234	955
ML-12-2	0.0235	968
ML-16.5-1	0.0234	955
ML-16.5-2	0.0234	960

*ML-4.5-1: Sample is from 4.5 meters below ground at multilevel well and samples were duplicated from each depth.

would be predicted for water in equilibrium with air(WEA).

At the Site 2, denitrification, if present, is confined to the overlying fertilized soils(Table 3). At the Site 1, much lower ratios reflect denitrification(Table 2). The Ar/N₂ ratios from the Site 1 form the lower level boundary for worldwide reported Ar/N₂ ratios. Water in equilibrium with air(WEA) has an Ar/N₂ ratios of 0.02670 at the same temperature(8 °C)

as these groundwater samples while the Ar/N₂ ratios of the Site 1 from 0.0148 to 0.0180(Table 2). These lower Ar/N₂ ratios can be explained by the production of nitrogen gas from active denitrification.

CONCLUSIONS

A method has been developed to simultaneously measure Ar⁺ and N₂⁺ beam and compute Ar/N₂ ratio using a VG isotopic ratio mass spectrometer. Measured Ar/N₂ ratios from air saturated water demonstrated the method to be accurate to within 0.2% of expected values. Method precision for air saturated water samples was 0.6%. The method was applied to extract groundwaters and the results were consistent for both groundwater areas with and without denitrification reported previously.

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