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A RAPID ON-LINE TECHNIQUE FOR THE DETERMINATION OF THE $\delta^{18}O$ and $\delta^{17}O$ OF GASEOUS AND DISSOLVED OXYGEN

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Molecular oxygen is a key component of the biosphere and hydrosphere and is essential to many life forms that live and reproduce in these environments. Numerous biogeochemical processes in soil, rivers, lakes and groundwater consume oxygen, and human impacts on these systems can have detrimental impacts. For example, in Canada industrial and sewage effluents discharged into northern boreal rivers have been shown to adversely affect dissolved oxygen (DO) conditions and affect aquatic biota, particularly under extended seasonal ice covered conditions [1].

Despite the importance of molecular oxygen in gaseous form or as DO in many hydrologic environments, there are relatively few studies that make use of the oxygen isotopic composition as a tracer of transport or biogeochemical processes in terrestrial and aquatic systems [2,3]. The isotopic composition of molecular oxygen may in fact be particularly suitable as such a tracer, as it does not readily undergo isotopic exchange with water or other gases [2], and so isotopic fractionation should mainly result from diffusive transport, biogeochemical consumption and abiotic oxidation-reduction processes, or from photosynthesis. Part of the reason for this lack of research is that the conventional offline technique of extracting and converting O_2 gas to CO_2 for isotopic analysis is time consuming, potentially fractionating, and considerable sample may be required to be transported and manipulated, especially for low oxygen content samples. The advent of continuous-flow isotope-ratio mass spectrometry (CF-IRMS) has reduced the large sample requirements of conventional dual inlet analysis by orders of magnitudes, and is especially suited to chromatographic gas separations and subsequent online isotopic analysis. The goal of this paper is to 1) demonstrate a field sampling protocol for gaseous and dissolved oxygen and 2) to outline a rapid, online GC-CF-IRMS analytical procedure to measure the $\delta^{18}O$ and $\delta^{17}O$ of O_2 gas. Preliminary data from field sites will also be presented to demonstrate the potential utility of oxygen gas isotope analysis as a tracer, and show a wide range of $\delta^{18}O_2$ values encountered in different environments in Canada.

Sample collection and preparation was a modification of the procedures outlined by [4], improved and modified to eliminate microbial activity and air contamination. In short, water or gas samples were drawn into sterilized, butyl septum crimp sealed (Bellco Biological Glassware, Vineland, NJ) serum bottles (250 cc, Wheaton # 2725) that were pre-evacuated to 0.001 atmospheres. Bottles for DO samples contained 100 μl saturated HgCl to fix bacterial activity. For DO sampling, a needle (21 G) was used to penetrate the septum while the sample vessel was submerged under water. For gas sampling, a 3-way valve was utilized to enable flushing of the needle with the sample gas to eliminate air contamination. Gas or water in the serum bottle was permitted to equilibrate for several minutes with the sample medium before the needle was withdrawn. After returning to the lab, a 3-way valve and needle system was used to dynamically flush the needle with helium prior to over-pressuring the sample vessel with 5-10 cc of 99.999% helium. Water samples were agitated on a wrist shaker for 1 hour to strip O_2 into the helium headspace. Between 500 μl and 3000 μl of headspace gas, depending on the O_2 concentration, were drawn into a 5 cc gas-tight syringe equipped with a second 3-way valve fitting that purged the needle with He to eliminate air contamination before sample injection into the GC-CF- mass spectrometer system, described below.

The $\delta^{18}O$ values of molecular oxygen in the atmosphere, gas and water samples were measured by GC-CF-IRMS using a Micromass Optima™, using pure O_2 as the reference gas. A Carlo Erba NA1500™ elemental analyzer was modified to accommodate a sample gas injection port after the combustion columns and prior to a CO_2 (ascarite) and water (Mg-perchlorate) trap and the GC column. The GC column used to resolve the remaining O_2 from N_2 was a 1m 5Å molecular sieve packed column held at 35°C. The separated O_2 sample pulse was then introduced to the mass spectrometer via an open split. The $\delta^{18}O$ and $\delta^{17}O$ values of sample oxygen were calculated by measurement of O_2 isotopes at m/z 34/32 and 33/32 and comparison to a reference pulse of O_2. Repeated injections of

99.999% research grade O_2 and atmospheric O_2 over a 3-week period yielded an external reproducibility of ±0.2 per mil for $\delta^{18}O$ and ±0.5 per mil for $\delta^{17}O$ (n= 29). Air oxygen was assumed to have a $\delta^{18}O$ value of +23.5 per mil (SMOW) and was subsequently used to correct sample and reference gas values. Instrument source linearity was excellent for O_2, exhibiting only a +0.5 permil shift over an air injection range size of 5000 μl to 200 μl (r^2=0.7, n=23). The smallest sample size for reliable $\delta^{18}O$ determinations by this technique was approximately 1 μmole of O_2. Total analysis run-time per sample is less than 2 minutes.

There are some significant advantages of the GC-CF-IRMS technique over conventional methods for O_2 isotopic measurements. First, the technique does not require cryogenic concentration of O_2 and subsequent conversion to CO_2 for analyses, thereby significantly reducing the possibilities of isotopic fractionation during sample preparation, which is particularly problematic with small samples. Second, samples are processed directly and very rapidly in contrast to the laborious and time consuming requirements of offline methods. Third, measurement of the $\delta^{18}O$ values of oxygen in the atmosphere, soil and water using O_2 as the analysis gas instead of CO_2 permits measurement of $\delta^{17}O$ values. Finally, the field collection and extraction technique is simple, inexpensive, and does not require the construction and use of costly vacuum manifolds for processing.

We will present current experimental laboratory and field results from soils and natural waters. A series of tests using this technique on air-saturated tap and distilled water confirmed the $\delta^{18}O$ isotopic fractionation factor of about +0.7 permil between air and water at ~20°C (n=8). A series of soil gas samples (n=50) taken through 30 meter thick unsaturated mining waste rock showed that combined biochemical consumption and gas transport processes in the subsurface can significantly fractionate O_2 isotopes. For example, $\delta^{18}O$ values ranged from air values just a few cm below ground surface +23.5 per mil (20.9 % O_2) to +45.5 per mil (1.4 % O_2) at depth. Preliminary data on under-ice riverine DO along a 1000 km transect of the boreal Athabasca River in Alberta show a trend of systematic $\delta^{18}O$ enrichment with decreasing DO saturation, indicating oxygen is being consumed. Conversely, under-ice photosynthesis (oxygen supersaturation) imparts a strongly depleted $\delta^{18}O$ signature to dissolved oxygen in the upper reaches of the Athabasca river.

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