

Spectrophotometric determination of alkalinity and pH in freshwaters

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The different compartments of the hydrosphere are major sinks or sources of CO₂ and the role of freshwaters in the global carbon cycle has been recently reevaluated as substantial [1]. Freshwaters show variations of the carbonate system variables at hourly time scales and in a large range. A key limitation for the carbonate system studies is the necessity of accurate, *in-situ* and high frequency measurements that would provide data with suitable spatial and temporal resolutions to enlighten the processes affecting the carbonate system.

With the aim of *in-situ* and high frequency sensor development to assess the freshwaters whole carbonate system with the simultaneous measurement of the pH-Alkalinity couple [2], spectrophotometric measurement of these parameters is developed. Spectrophotometric pH measurements already exist [3] this work focuses mainly on the alkalinity (Alk) measurement, which is an original contribution. This new method, based on [4], consists to neutralize all the basic species taken into account in the Alk by a weak acid mixed with a pH sensitive dye to measure accurately the pH end point value and thus deduce the alkalinity of the sample.

The performance of spectrophotometric methods is assessed in low pH buffer solutions for pH, commercial mineral and spring waters for Alk and natural freshwaters for both, by a comparison to conventional potentiometric measurements and theoretical calculations.

pH measurements show a precision of ± 0.005 and an accuracy of 0.01 pH unit; Alk measurements show a precision of $\pm 8 \mu\text{M}$ and an accuracy ranging from 19 to 2 μM . The best accuracy is obtained by downplaying the excess acid term and thus its associated uncertainty. Additionally, accuracy relies upon the performance of the spectrophotometer, carefully prepared and defined indicator solution and all very controlled and reliable thermodynamic constants with their temperature and ionic strength dependence. The somewhat poorer precision reported might be ascribed in a larger part to the totally handmade procedure steps that introduce more errors than an automatic device. Tests on our pH and Alk *in-situ* sensor (still in development), shows that a precision better than ± 0.001 unit on pH and better than $\pm 2 \mu\text{M}$ on Alk are expected.

This work provide a strong theoretical basis for its future use as an *in-situ* high frequency sensor, which precision and accuracy meet the requirements of scientist working on freshwaters systems.

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[2] Park (1969) *Limnol. Oceanogr.* **14** (2), 179-186.

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[4] Podda (1994) *Compt. R Acad. Sci.*, **319** (2), 651-657

Using Noble Geochemistry to Identify the Genetic Fingerprint of Natural and “Fugitive Gases” in the Marcellus Play of Northern Appalachian Basin

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Abstract

Osborn et al [1] recently reported 17-times higher concentrations of thermally mature methane (CH₄), consistent with production gases from the Marcellus shale, in drinking water wells within 1km of hydraulically fractured horizontal drilling sites producing from the Marcellus Shale in northeastern Pennsylvania. We employ a combination of hydrologic (groundwater age dating [³H-³He and fluid flow modeling]), noble gas geochemistry, and carbon isotopic composition to distinguish the potential sources of gases present in drinking water aquifers within the region. These techniques simultaneously distinguish Marcellus/Devonian gas from deeper Trenton Group/Ordovician gases and other potential sources (e.g. shallow biogenic methane, stray landfill gases, other organic-rich lithologies, and natural gas that has migrated naturally over geologic time) providing a powerful technique for delineating the source and potential for fugitive gas migration in areas active or targeted for drilling. We will present preliminary results of noble gas and isotope geochemistry for Pennsylvania and New York areas of the Marcellus fairway.

[1] Osborn SG, Vengosh A, Warner NR, & Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences* 108:8172-8176.