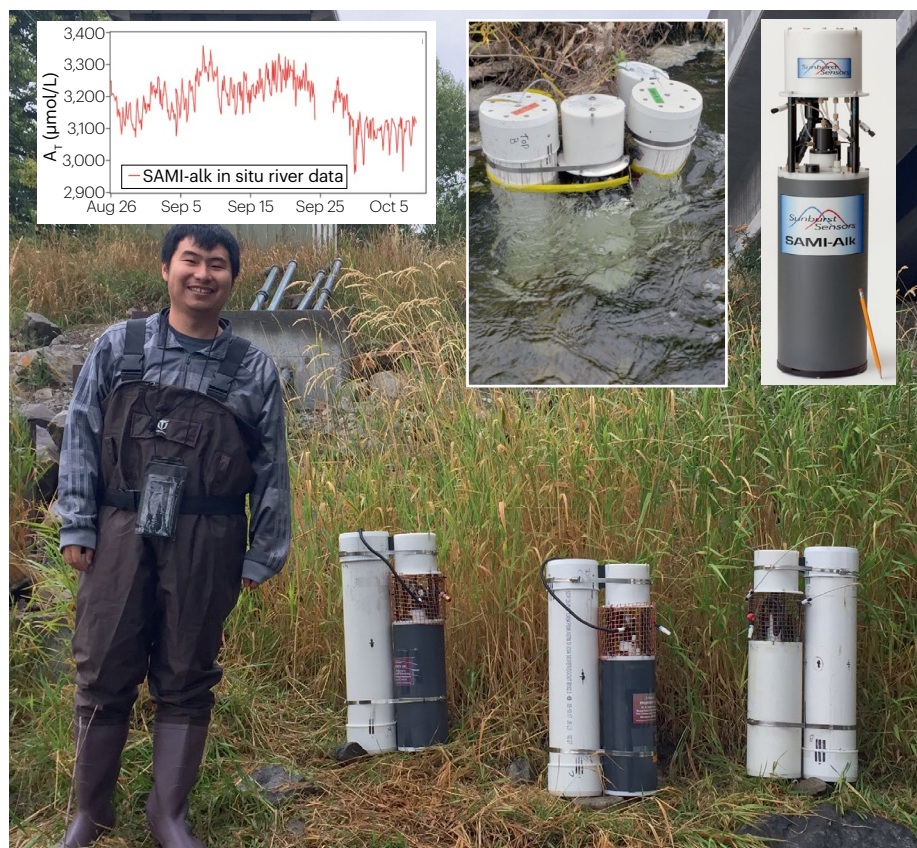


Remote autonomous titration



Titration is an analytical method where a solution of known concentration, the titrant, is used to react with an analyte of unknown concentration. In a typical titration, the titrant is sequentially added to the sample until an endpoint is reached where the analyte is entirely consumed. This endpoint is commonly detected by a change in colour. Titration methods, also named titrimetry, have been around for a long time. One of the first titrations, reported in 1729, measured the concentration of acetic acid in vinegar by step-wise addition of a strong base. It was quickly realized that unequalled precision and accuracy could be obtained by careful volumetric addition of a titrant using a calibrated burette. Hundreds of types of titrations have been developed since that time, reflecting titrimetry's exceptional accuracy, selectivity, and versatility. Today, it is not only a rite of passage for undergraduate chemistry students but remains widely used

in industry and environmental monitoring because of its superior performance.

These days most titrimetric systems are automated for routine analyses. They use accurate liquid dispensers such as syringe pumps or automated burettes, and synchronous electrochemical or spectrochemical detection that is compatible with an auto-sampler. One shortcoming of these systems, however, is that they are not able to operate outside of a pristine laboratory setting. There are many chemical monitoring applications where in situ or in-line monitoring are needed. Natural waters, for example, can be impacted by episodic events such as storms or algal blooms that might be missed by periodic sampling.

Our research is focused on the development and application of in situ instruments for autonomous measurements in natural waters. We developed an in situ alkalinity titration system that uses an indicator to

track the pH and amount of hydrochloric acid added to the sample in a stirred optoflu-idic cell. This system – named the Submers-ible Autonomous Moored Instrument for alkalinity, or SAMI-alk – can be deployed in marine and freshwater environments for a couple of months at a time, making meas-urements every hour. It is, to our knowledge, the first system to perform titrations in situ.

This innovative strategy uses the pH indicator to not only determine pH but to also quantify the amount of titrant added, eliminating the need for a complicated and bulky automated burette or syringe pump. Instead, SAMI-alk uses small, low-tech sole-noid pumps to dispense the indicator and acid mixture.

Alkalinity, which is the amount of titrat-able base in water, is important in these systems because it gives insights into the source of water, extent of buffering, and if calcium carbonate formation occurs (particularly in coral reefs). The freshwater field studies revealed that alkalinity varies on short (<1 day) timescales due to storm runoff events and transpiration by riparian (stream side) vegetation – a process that regulates the daily groundwater flow into a river (see plot in image).

The SAMI-alk can also be used with the SAMI-pH technology, an indicator-based pH measurement system. These combined measurements make it possible to fully quantify the inorganic carbon species in water (such as CO_2 , HCO_3^- and CO_3^{2-}). With combined pH and alkalinity measurements, metal speciation and solubility can be estimated. This informa-tion is particularly valuable for mine-waste-polluted rivers – a problem commonly encountered in Montana, USA. We hope that with more widespread use of autonomous measurement technology our understand-ing of human impacts on natural waters will continue to improve.

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Competing interests

The author declares no competing interests.