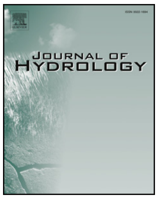
Journal of Hydrology 561 (2018) 267–276

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol



Research papers

Analysis of metal-laden water via portable X-ray fluorescence spectrometry

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ARTICLE INFO

This manuscript was handled by P. Kitanidis, Editor-in-Chief, with the assistance of Pedro J. Depetris, Associate Editor

Keywords:
PXRF
Water analysis
Metals

ABSTRACT

A rapid method for in-situ elemental composition analysis of metal-laden water would be indispensable for studying polluted water. Current analytical lab methods to determine water quality include flame atomic absorption spectrometry (FAAS), atomic absorption spectrophotometry (AAS), electrothermal atomic absorption spectrometry (EAAS), and inductively coupled plasma (ICP) spectroscopy. However only two field methods, colorimetry and absorptiometry, exist for elemental analysis of water. Portable X-ray fluorescence (PXRF) spectrometry is an effective method for elemental analysis of soil, sediment, and other matrices. However, the accuracy of PXRF is known to be affected while scanning moisture-laden soil samples. This study sought to statistically establish PXRF's predictive ability for various elements in water at different concentrations relative to inductively coupled plasma atomic emission spectroscopy (ICP-AES). A total of 390 metal-laden water samples collected from leaching columns of mine tailings in South Africa were analyzed via PXRF and ICP-AES. The PXRF showed differential effectiveness in elemental quantification. For the collected water samples, the best relationships between ICP and PXRF elemental data were obtained for K and Cu ($R^2 = 0.92$). However, when scanning ICP calibration solutions with elements in isolation, PXRF results indicated near perfect agreement; Ca, K, Fe, Cu and Pb produced an R^2 of 0.99 while Zn and Mn produced an R^2 of 1.00. The utilization of multiple PXRF (stacked) beams produced stronger correlation to ICP relative to the use of a single beam in isolation. The results of this study demonstrated the PXRF's ability to satisfactorily predict the composition of metal-laden water as reported by ICP for several elements. Additionally this study indicated the need for a "Water Mode" calibration for the PXRF and demonstrates the potential of PXRF for future study of polluted or contaminated waters.

1. Introduction

Clean water is one of the most common, yet essential compounds required for life of countless organisms. Often, water has various elements (e.g., Ca, Mg, Cl, F) dissolved in it which pose little concern to organisms so long as concentrations are relatively low. When concentrations of dissolved salts become too high, the water is often termed brackish or salt-water. High concentrations of dissolved metals in water can pose a serious public health risk as such substances are commonly non-detectable without laboratory analysis. In some instances, the metals dissolved in water come from natural geologic sources. For example, Berg et al. (2001) found As levels in raw groundwater used to supply Hanoi treatment plants often surpassed World Health Organization (WHO) limits of 10 μg L^{-1}, the origins of which stem from the Red River Basin. Nordstrom (2002) detailed an extensive list of countries with As-laden groundwater including Bangladesh, India, Argentina, Chile, Germany, Hungary, Romania, USA, and many others whereby As is naturally occurring from geologic sources. In other cases the metals stem from industrial pollution, mining, or waste migration into surface or subsurface waters used for drinking. For example, smelting operations in Eastern Europe left widespread metal pollution across surface soils (Paulette et al., 2015; Weindorf et al., 2013). Similarly, Razo et al. (2004) found surface water storage ponds in Villa de la Paz-Matehuala contained As levels more than five times the Mexican drinking water standard. More recently in the United States, the city of Flint, Michigan (pop. ~100,000) experienced a public health crisis when the city's water supply became contaminated with Pb (Hanna-Attisha et al., 2016). In 2015, the Gold King Mine spill in Colorado, USA released hundreds of thousands of gallons of acid mine drainage waste into the Animas River; a source of irrigation water for the farming

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https://doi.org/10.1016/j.jhydrol.2018.04.014
Received 5 January 2018; Received in revised form 20 March 2018; Accepted 4 April 2018

communities of Farmington, New Mexico and the Navajo Nation (Rodriguez-Freire et al., 2016). Some studies have also established linkages between metal content in water and other chemical factors such as pH (Muhammad et al., 2011) and conductivity (Kar et al., 2008).

The WHO (2008) has established numerous chemical limits for various elements in drinking water in order to assure human health and safety. For example, the WHO drinking water guidelines for Pb, Zn, and Cu are 10 μg L^{-1}, 3 mg L^{-1}, and 2 mg L^{-1}, respectively. In determining water quality, the WHO reviews a number of analytical methods, among them flame atomic absorption spectrometry (FAAS), atomic absorption spectrophotometry (AAS), electrothermal atomic absorption spectrometry (EAAS), and inductively coupled plasma mass spectroscopy (ICP-MS). By comparison, only two field methods are noted: colorimetry and absorptiometry. Thus, fewer field methods are available and with less analytical precision and accuracy, relative to laboratory approaches.

Recently, portable X-ray fluorescence (PXRF) spectrometry has rapidly developed as a field-portable instrument capable of producing multi-elemental data with limited sample preparation. The Royal Society of Chemistry (2009) provides a succinct overview of the technology whereby a miniature X-ray tube dissipating a few watts is used to excite elements, thereby causing them to generate secondary fluorescence X-rays with characteristic energies for each element. Elemental abundance is quantified via silicon drift detector (SDD), which provides “higher resolution with little degradation in spectrum quality (e.g., count rate-dependent peak broadening or drift)” relative to silicon PIN detectors (Royal Society of Chemistry, 2009). Matrix interference is caused by inter-elemental effects whereby emission line overlap and other background variation must be resolved through signal processing (Peinado et al., 2010). While PXRF is theoretically capable of determining many elements, the excitation of low atomic number elements (e.g., < K) is often problematic given fluorescence attenuation in air. Helium purge or vacuum attachments can overcome some of these limitations, but PXRF determination on low atomic number elements remains problematic (Weindorf et al., 2014). Those limitations notwithstanding, numerous methods now exist for PXRF evaluation of elements in soil and sediment (US-EPA, 2007; Soil Survey Staff, 2014; Weindorf and Chakraborty, 2016). A litany of studies have established its use for soil (e.g., McLaren et al., 2012a; Zhu et al., 2011; Chakraborty et al., 2017a) and vegetal analysis (e.g., McGladdery et al., 2018; McLaren et al., 2012b; Reidinger et al., 2012). However, the evaluation of liquids by PXRF is comparatively sparse. An early study by Eksperiandova et al. (2002) evaluated wastewater by PXRF using agar and gelatin as a holding matrix for polluted waters. They obtained reasonably low relative standard deviations (up to 0.08%) for several metals at low concentrations (< 400 mg L^{-1}). Pearson et al. (2017) extended the use of PXRF by directly determining water salinity based upon elemental determinations of brine waters in a hooded test stand. Using piecewise linear regression of PXRF sensed Cl, they obtained R^2 values of 0.77 (RMSE 0.95 μS cm^{-1}) relative to electrical conductance. Further unpublished data by Pearson et al. investigated the utility of PXRF to quantify metals in standard ICP calibration solutions. Results showed the potential for multi-elemental determination with accuracy of ~ ± 10% relative to certified reference values.

Several well-known limitations do exist for PXRF, one of which specifically relates to moisture causing fluorescence attenuation (Weindorf et al., 2014). Further, it is well established that PXRF cannot attain the low limits of detection nor precision offered by ICP or other laboratory-based instrumentation. Contrariwise, PXRF offers speed, portability, and reasonable accuracy that may far surpass current field techniques such as colorimetry. Even if PXRF was able to effectively differentiate remarkable from non-remarkable samples for certain elemental concentrations in solution, it would still remain a formidable advance over current techniques, one which could potentially save both time and money.

Given the rapid advancements of PXRF for chemical analysis in numerous matrices, its evaluation for direct assessment of polluted water seems timely. As such, the objective of this study was to statistically establish PXRF’s predictive ability for various elements in water at different concentrations relative to ICP. We hypothesize that PXRF will aptly quantify numerous elements in water at concentrations of 10–10,000 mg L^{-1}.

2. Materials and methods

2.1. Sample collection

A total of 390 water samples were collected from leaching columns of mine tailings in South Africa. Leaching of the tailings was generally in accordance with Method D5744-13 (ASTM, 2013). With deference and respect to maintaining mine operator anonymity, the exact mines sampled cannot be disclosed. However, they were generally an assortment of Cu, U, Zn, Ag, and Au mines. In addition to common soil mineral matrices (e.g., montmorillonite, biotite, quartz, calcite, hematite, gypsum, muscovite), substantive concentrations of more exotic minerals (e.g., gahnite, sphalerite, galena, nchwaningite, uranopolycrase, billietite, chlorargyrite, cuprospinel) were found (as confirmed by X-ray diffraction) in the tailing samples subjected to leaching. Prior to leaching, each tailings sample was ground to < 6 mm and placed in a column. Each column was leached with 750 ml of deionized water, then preserved with HNO_3 and stored in clean, sealed bottles at 4 °C. Samples were then transported to Texas Tech University (Lubbock, TX, USA) for analysis in the Pedology laboratory.

2.2. Laboratory analysis

Prior to analysis, samples were allowed to return to room temperature (20 °C). Any samples containing suspended particles were filtered with #2 filter paper (Micro Filtration Systems, Dublin, CA, USA) before analysis. Each sample was placed in a Series 1400 plastic sample cup (Chemplex Industries, Palm City, FL, USA), then covered with Prolene® thin-film (Chemplex Industries, Palm City, FL, USA) (Fig. 1). A Delta Premium (DP-6000) PXRF (Olympus-Innov-X; Waltham, MA, USA) was calibrated with a standard 316 metal alloy target prior to scanning the samples. PXRF instrument performance was validated via the scanning of multiple ICP standards. The PXRF was stationed in a proprietary test stand (Fig. 2), that shields the user from errant X-rays, and the sample cups were place on the sample stage and inverted directly over aperture of the PXRF (Fig. 2). The instrument was set to Soil Mode and configured to scan each sample with three 30 s beams, totaling 90 s of scanning per sample (Weindorf and Chakraborty, 2016).

Fig. 1. Water samples placed in Series 1400 plastic sample cups and covered with Prolene® thin-film.