Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 66 (2005) 961–966
Talanta
www.elsevier.com/locate/talanta

Colorimetric detection of uranium(VI) on building surfaces after enrichment by solid phase extraction

Philip A. Greene[a], Christine L. Copper[a], David E. Berv[b], Jeremy D. Ramsey[b], Greg E. Collins[c,*]

[a] United States Naval Academy, Chemistry Department, 572 Holloway Road, Stop 9b, Annapolis, MD 20639, USA
[b] GeoCenters, Inc., Suite 200 Ballston Station, 4301 N. Fair Arlington, VA 22201, USA
[c] Naval Research Laboratory, Chemistry Division, Code 6112, 4555 Overlook Ave., S.W., Washington, D.C. 20375-5342, USA

Received 18 October 2004; received in revised form 17 December 2004; accepted 17 December 2004

Abstract

A method for detecting and quantifying uranium(VI) levels on building materials that include concrete, Plexiglas, glass and steel surfaces is presented. Uranium(VI) was extracted from building material surfaces using a pH 2.2 buffer rinse and, subsequently complexed by an organic chelating agent, arsenazo III. The application of a uranium-chelating molecule, arsenazo III, allows for concentration enhancement using C_{18} solid phase extraction and colorimetric detection of the uranium complex using ultraviolet–visible spectroscopy at 654 nm. The method has a detection limit (based on 3σ) of 40 ng/L (5 ng/cm^2) and an overall extraction efficiency greater than 80% for each surface type (concrete, Plexiglas, glass, steel). Methods to prevent interference by metal ions commonly found on building materials are discussed.

Keywords: Uranium (VI); Arsenazo III; Solid phase extraction; Building materials

1. Introduction

The United States Department of Energy (DoE) has been involved in the development and production of nuclear weapons and nuclear fuel since the early 1940s. As a legacy of this work, there are thousands of DoE buildings across the US that are contaminated by radionuclide and heavy metals, including uranium(VI). The DoE is responsible for decommissioning these sites in a manner that is environmentally acceptable through a project called Superfund [1]. Over 7000 buildings and structures are no longer in use by the DoE and have now become the focus of the Superfund program due to either confirmed contamination or a high probability of contaminated materials. Although Superfund is not specifically focused on radiological contamination, considerable portions of the Superfund sites covered by this program are thought to contain radiological waste. The DoE faces the task of surveying these sites to determine what materials within them require special disposal considerations and what materials are safe for normal disposal methods. Completing this task in an accurate and timely fashion is essential to the preservation of the environment and the minimization of decommissioning costs.

Currently, confirmation of radionuclide contamination by the DoE is done by scintillation and inductively coupled plasma mass spectrometry (ICP/MS) in the laboratory, and, for field use, Geiger counters and X-ray fluorescence (XRF) [2–5]. While scintillation and ICP/MS are quite sensitive and effective as detection methods, they require the technical operation of expensive pieces of laboratory instrumentation. Because the instrumentation is not field portable, samples must be collected and shipped off for analysis at off-site laboratories, significantly delaying decommissioning efforts. Geiger counters, although field portable and capable of indicating the presence or absence of radioactive materials at a site, are not element specific and merely count the radioactive events over time. Many remediation efforts and Environmental

---

* Corresponding author. Tel.: +1 202 404 3337; fax: +1 202 404 8119.
E-mail address: gcollins@ccf.nrl.navy.mil (G.E. Collins).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.12.061

Protection Agency (EPA) protocols depend upon the accurate knowledge of the specific metal ion and concentration before any action can be pursued with regards to either disposal or clean-up procedures. Field portable XRF spectrometers are commercially available, and their use as a screening tool for elemental concentration in soil is outlined in an EPA method [5]. Although XRF has the advantage of providing a rapid, non-destructive, elemental composition of surfaces, the detection limits are on the order of 100 mg/kg (ppm) and the instrumentation can be quite expensive (ranging from $60,000 to $90,000 per instrument). Furthermore, the method recommends a minimum of 5% of the samples tested by XRF be confirmed by EPA analytical laboratory methods, which require partial or total sample digestion prior to measurement [6,7].

Solid phase extraction (SPE) is a commonly used technique in the sample preparation steps of many analytical methods. Many silica or alumina beads functionalized with polar, non-polar, or ionic groups are available for use in preconcentration and extraction. SPE is used to enhance the selectivity and/or the sensitivity of a method as it allows for discriminatory binding of analyte to a solid support where it can be amassed and subsequently eluted with a smaller volume of solvent. The result of this process is a solution that contains a higher concentration and purity of the analyte.

The goal of this work was to investigate a non-invasive, inexpensive, and simple method for detecting uranium(VI) on building materials, with the future intention of implementing a field portable detection system. Arsenazo III, a non-specific chromogenic reagent, was selected as the complexing agent for facilitating uranium(VI) detection via ultraviolet–visible (UV/vis) spectroscopy. Previously, arsenazo III has been used for the detection of various metal ions, including uranium(VI), and its behavior is well understood and documented [8,9]. However, the non-specific nature of arsenazo III complexation can lead to interferences from the high concentration of metal ions in building materials [10]. Therefore, careful control over sampling conditions, such as wash buffer pH, was needed. By minimizing the binding of competing metal ions with arsenazo III, it was possible to isolate and preconcentrate the hydrophobic uranium:arsenazo III complex using C_{18} solid phase extraction (SPE), leading to a simple but very sensitive method for quantitation of uranium levels on various building material surfaces. In addition, the method described here utilizes a sampling method that literally dissolves the surface layer of concrete, giving a more quantitatively useful screening method for examining porous concrete, than other surface sensitive probes.

2. Experimental

2.1. Reagents

Arsenazo III and disodium ethylenediaminetetraacetic acid (EDTA) were obtained from Sigma–Aldrich (St. Louis, MO). The uranium stock solution (985 μg/mL in 1% nitric acid) was an atomic absorption standard acquired from Spex (Metuchemn, NJ). All other reagents and the SPE columns (300 mg of C_{18}-modified silica gel) used were obtained from Fisher Scientific (Vernon Hill, IN). Although there are a variety of stationary phases available with ranging polarity and chemical structure, the C_{18} SPE material was selected because of previous success observed for the hydrophobic extraction of organic metal chelates [11,12]. All water used was ultra-filtered and had an electrical resistance greater than 18 MΩ (Millipore). Stainless steel plates (11 cm × 16 cm × 1 cm) and concrete samples (~5 cm^3) from the Idaho National Engineering and Environmental Laboratory (Idaho Falls, ID) were provided by the DoE. Additional concrete and poly(methyl methacrylate) (commonly known as Plexiglas®) samples (5 cm × 5 cm × 0.3 cm) were acquired from a local source and used without modification.

2.2. Sampling technique

A known volume of uranium stock solution was added to 125 μL of ethanol (giving concentrations between 10 (1.5 μg) and 100 mg/L (12 μg)) and pipetted onto a planar sample surface area of approximately 8 cm^2. The effective surface area of concrete exposed to uranium is actually greater than 8 cm^2, due to its porous nature. The surface was then allowed to dry, creating a uranium(VI) contaminated sample for analytical method development and testing. Using 25 mL of 0.020 M malonic acid buffer at a pH of 2.2, the entire face of the sample was washed into a collection beaker. Five milligrams of EDTA solid and 40 mL of a 1 mM arsenazo III stock solution prepared in malonic acid buffer were added to the wash solution. The solution was then vacuum aspirated through a C_{18} SPE column that had been previously conditioned stepwise using 20 mL each of 0.1 M HCl, water, and methanol. The hydrophobic uranium(VI):arsenazo III complex was visibly retained as a blue-purple band. Following loading, a 20 mL volume of water was drawn through the column to remove any weakly bound arsenazo III. The concentrated uranium(VI):arsenazo III complex was eluted from the column by manually forcing 200 μL of methanol through the column using a syringe and collecting the eluent in a graduated micro-vial. To maintain a reasonable absorbance, the concentrated sample was diluted to 600 μL with the same malonic acid buffer used above. Due to the toxicity of methanol, special care should be taken in handling this organic solvent.

2.3. Apparatus and data analysis

The UV/vis spectra were obtained using a Cary 3C spectrophotometer (Varian, Walnut Creek, CA) using a 0.6 mL thin layer absorbance cell with a path length of 1 cm (Spectrocell; Oreland, PA). The absorbance of each sample was measured at 1 nm intervals using light with wavelengths between 400 and 800 nm. Analysis of the spectra was performed using the GRAMS/32 software package (Thermo Galactic; Woburn, MA). Even though the desired absorption band was red-shifted from the free dye, the desired absorption band still rested on a sloping baseline due to the free arsenazo III absorbance. To remove the effect of the baseline on the measured absorbance, the GRAMS/32 peak analysis module was used to select approximate peak centers (either manually or automatically), after which a Gaussian curve-fitting algorithm was used by the software to accurately identify individual absorbance bands. The fitting routine was allowed to converge and the results were confirmed visually prior to data analysis. Following curve fitting, the areas beneath each band were recorded along with peak height, full width at half height, and the wavelength at which each peak was centered. Peak areas produced calibration curves with a higher degree of linearity than peak heights and were utilized throughout this study.

3. Results and discussion

Concrete varies in composition based on the source of the sand and stones it contains, as well as the composition of the cement that holds the sand and stones together [13]. Generally, calcium carbonate is the primary component evident in cement. Other cations such as aluminum, magnesium, and iron are also commonly found in concrete samples [13]. Due to the high concentration of metal ions present in concrete, any method for verifying radionuclide contamination must be tolerant toward high concentrations of possible interfering cations.

Arsenazo III is useful as a detection agent for uranium because its absorbance significantly red shifts when complexed by uranium at pH 2.2 (Fig. 1). Uncomplexed arsenazo III has a strong absorbance at 540 nm (Fig. 1A) that red-shifts to 654 nm upon complexation by uranium(VI) (Fig. 1B). A drawback of using arsenazo III for uranium detection, however, is that it readily binds other, more common metal ions, also causing a red shift in absorbance.

Most troubling to this investigation, calcium is the most abundant metal cation contained in concrete [13], and the calcium:arsenazo III absorbance (654 nm) directly overlaps the uranium:arsenazo III signal at pH values above 4.0 (Fig. 1C). Fig. 2 illustrates the reduction of calcium:arsenazo III binding as a function of pH at 654 nm. As seen in the figure, the interference from calcium is prevalent at the higher pH values, while inversely, uranium binds more strongly to arsenazo III at lower pH. Fortunately, arsenazo III binding of calcium and other cations contained in concrete can be essentially eliminated by buffering the sample solution to a pH of 2.2 and adding EDTA as a competitive complexation agent. Near pH 2, arsenazo III binds strongly to uranium (predominantly UO_2^{2+}) with maximum absorbance [9], while the absorbance due to calcium is greatly diminished.

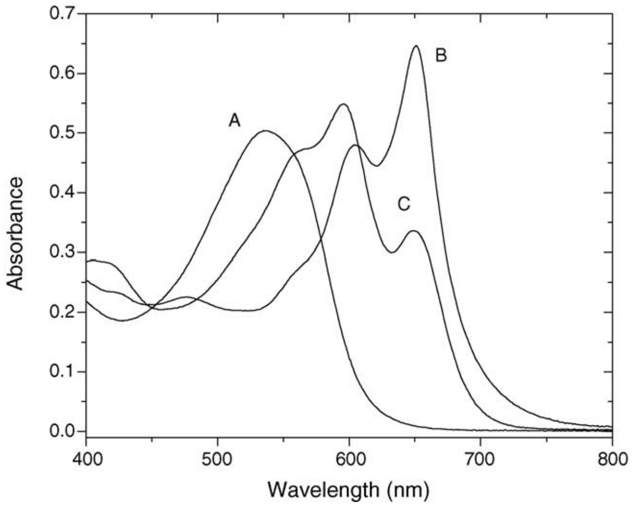

Fig. 1. Absorbance spectra of arsenazo III and its metal complexes measured at pH 2.2: (A) free arsenazo III, (B) uranium:arsenazo III complex, (C) calcium:arsenazo III complex. Analyte concentrations: [U(VI)] = [Ca^{2+}] = 500 μg/L, [Arsenazo III] = 10 mg/L.

Fig. 3A shows the absorbance spectrum for the arsenazo III complexes formed with other metal ions commonly found in cement at pH 2.2. As the spectra in Fig. 3A illustrate, these metal complexes have no absorbance band near 654 nm, indicating a lack of binding with arsenazo III at pH 2.2. Consideration of interferants is especially important because the malonic acid buffer rinse actually dissolves the surface layers of concrete. Therefore, the rinse solution contains not only the surface confined uranium, but also any constituents or contaminants from the sample surface. Other radionuclides such as cerium and thorium will produce a red shift in the arsenazo III absorbance (Fig. 3B), inflating the measurement of uranium. Because the concrete at Superfund sites is thought to be contaminated by a number of other

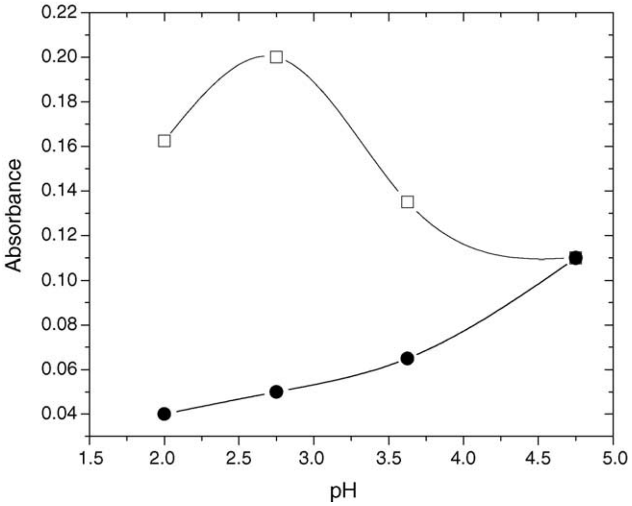

Fig. 2. The effect of pH on the 654 nm absorbance of arsenazo III complexed with uranium (open square) and calcium (solid circle) in mildly acidic solutions. The analyte concentrations are the same as in Fig. 1.

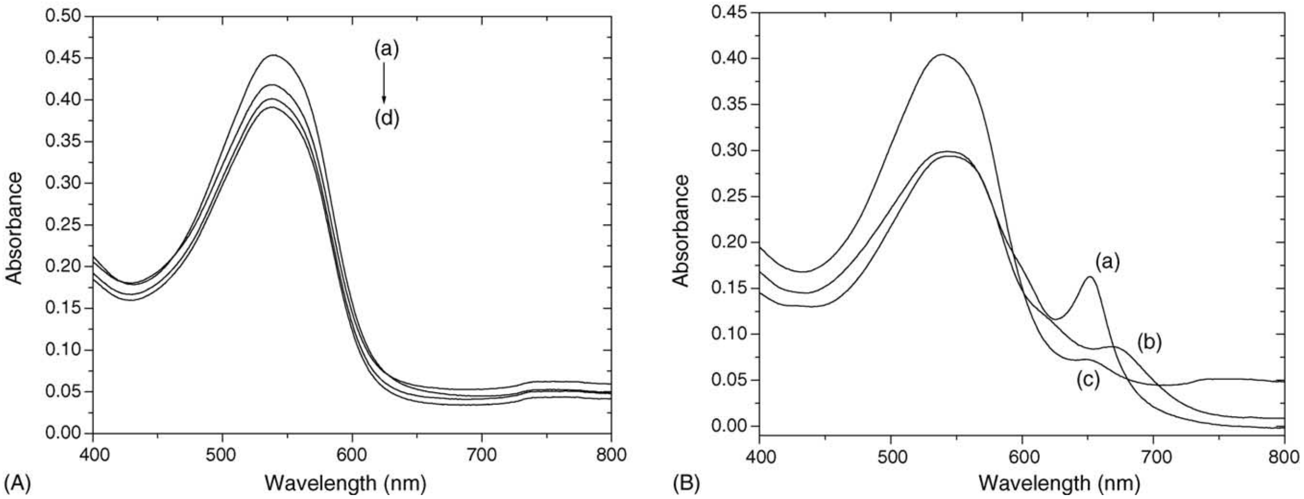

Fig. 3. Absorbance of various cation:arsenazo III complexes expected washing of building material surfaces (washed and measured at pH 2.2): (A) calcium (a), magnesium (b), iron (c), and aluminum (d); (B) uranium (a), thorium (b), and cerium (c). Analyte concentrations: [cation] = 500 μg/L, [Arsenazo III] = 10 mg/L.

radionuclides [1] and the absorption profiles of the arsenazo III complexes are similar, an additional separation method such as capillary electrophoresis may be necessary for determination and quantitation of individual radionuclides [14].

Since the amount of uranium expected on building material surfaces is likely small, it is important that the washing and extraction procedures maintain high efficiencies to allow for sufficiently low detection limits. To quantitate our ability to remove uranium from surfaces, we define washing efficiency as the ratio of the uranium:arsenazo III complex absorbance (as a peak area) of a solution extracted from building material to a solution in which the quantitative amount of uranium is added directly. It is unclear what form uranium will possess when adsorbed to building material or its spatial location, however, it has been shown that for concrete, uranium will only slowly diffuse into the porous network, with the majority still residing in the outer surface layers even after 50 years [15]. Although there is incorporation of uranium into the concrete structure, the acidic rinse utilized here actually dissolves the surface layers via protonation of carbonate, liberating the bulk of the uranium from the surface. Hydroxides and carbonates of uranium have high solubility at low pH as well [16]. Because of these factors, the washing efficiency for concrete surfaces was found to be extremely high, nearly 94% (Table 1).

Plexiglas, glass, and steel have surface chemistries markedly different than that of concrete. The surface of these materials is non-porous, and incorporation of uranium is unlikely. In these situations, it is more likely that adsorbed uranium will be in the form of soluble salts, all of which can be readily rinsed from the surface. As with the concrete samples, the washing efficiency was found to be very high, with values exceeding 88% for each type of building material (Table 1).

A non-polar C_{18} stationary phase was employed as a SPE bed for retaining the uranium:arsenazo III complex in the rinse solution and increasing the complex concentration prior to detection. The complex forms in a ratio of one arsenazo III molecule to one uranium ion under mildly acidic conditions (pH 1–3) [9], with the arsenazo III providing sufficient hydrophobic character to allow retention of uranium from aqueous solution onto a C_{18} column. In this sense, the SPE column was selective for cations that bind to arsenazo III at pH 2.2, due to the hydrophobicity of the organic chelate. Consequently, calcium and other unbound metal ions were unretained by the column and washed away during the rinse phase, providing further redundancy in the minimization of interferants. Most importantly, SPE enabled the uranium:arsenazo III complex to be eluted into a small eluent volume at a significantly enhanced concentration. Prior to analysis, the effective concentration of uranium in the sample solution was

Table 1
Comparison of efficiencies from uranium-spiked building materials[a]

	Wash efficiency (%)	Solid phase extraction efficiency (%)	Overall efficiency (%)
Concrete	93.6 ± 5	93.0 ± 3.5	87.0
Steel	88.7		82.5
Plexiglas	89.2 ± 8		82.9
Glass	92.3 ± 8		85.8

[a] Surfaces spiked with 125 μL of uranium containing solutions with concentrations between 10 (1.5 μg) and 100 mg/L (12 μg).

Table 2
Comparison of results from uranium-spiked building materials

	Surface concentration range (μg/cm^2)	Linear fit (R^2 value)	Limit of detection (3σ; ng/cm^2)
Concrete	0.187–1.50	0.998	5.8
Steel	0.937–1.88	0.980	6.1
Plexiglas	0.876–1.64	0.982	6.0
Glass	0.189–1.42	0.979	5.8

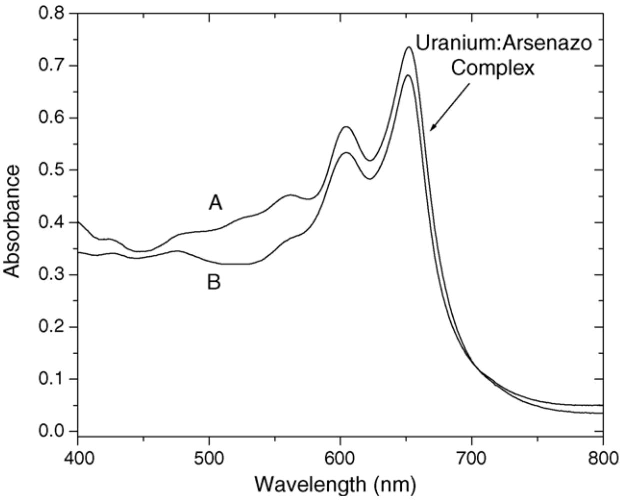

Fig. 4. Absorbance spectra of uramium:arsenazo III complexes following washing from (A) Plexiglas and (B) concrete. The uranium surface concentration was 1.85 μg/cm^2 (14.8 μg over surface area tested).

increased by a factor of 325. The efficiency of the extraction process was determined by comparing the peak area measured from a buffered uranium:arsenazo III solution that was passed through the extraction process to one that was not. The extraction efficiency was found to be 93.0% for each surface, indicating that very little uranium complex was retained irreversibly by the C_{18} column.

As seen in Table 1, the overall extraction efficiencies were quite high, with total method efficiencies well above 80%. Spectra of uranium extracted from concrete and stainless steel surfaces are contained in Fig. 4 and indicate the ability to observe small amounts of uranium adsorbed to building materials. Surfaces that were not spiked with uranium showed no absorbance at 654 nm (not shown) and had spectra similar to those in Fig. 3A. For the determination of uranium on concrete surfaces, the measured absorbances (654 nm) were linear ($R^2 = 0.998$) over the entire range of uranium surface concentrations studied (0.187–150 μg U/cm^2). The calibration curves for uranium-spiked steel, Plexiglas, and glass were also linear with correlation coefficients between 0.98 and 1.00. The calibration statistics for all of the building materials are included in Table 2. The theoretical detection limit of this method, based on three times the standard deviation of the blank absorbance at 654 nm, was determined to be 40 ng/L or 5 ng/cm^2 on a surface building material. This detection limit is 750 times lower than the EPA drinking water standard for uranium (30 μg/L), and is expected to be below the natural level of uranium in geologic materials [15] (note: uranium is not naturally contained in steel or Plexiglass). A practical detection limit on the order of 300 ng/L (100 ng/cm^2) was found via experimental data obtained from concrete.

4. Conclusions

A simple, non-expensive, non-destructive method for the detection and quantification of uranium(VI) was developed. Using this method, samples can be quickly obtained and analyzed, giving results in a much shorter time than available from previous methods of detection. With an experimental detection limit 750 times lower than the EPA drinking water standard, detection of small amounts of deposited uranium can be realized. By altering the conditions for sampling and testing of the sample, competitive binding by other metal ions with arsenazo III was minimized.

Acknowledgements

The authors would like to thank Dr. Qin Lu for useful discussions during preparation of this manuscript. Financial support for this work was provided by the Environmental Management Science Program of the Department of Energy and the Naval Academy Research Office.

References

[1] Available from: http://www.epa.gov/superfund/, “U.S. Environmental Protection Agency: Superfund” cited April 29, 2004.
[2] G. Kuppers, G. Erdtmann, J. Radioanal. Nucl. Chem. 210 (1996) 65.
[3] K. Kato, M. Ito, K. Watanabe, Fresenius J. Anal. Chem. 366 (2000) 54.
[4] Z. Papp, S. Daroczy, J. Radioanal. Nucl. Chem. 181 (1994) 413.
[5] Portable X-Ray Fluorescence Spectrometer; DoE/EM-0402, OST Reference #1790; U.S. Department of Energy, Office of Environmental Management, 1998. Section 1, pp. 1–3.
[6] USEPA Method 3050b, Acid Digestion of Sediments, Sludges, and Soils; Report No. SW-846 Ch 3.2; US Environmental Protection Agency, December 1996.
[7] USEPA Method 3052, Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices; Report No. SW-846 Ch 3.2; US Environmental Protection Agency, December 1996.
[8] M. Macka, P.R. Nesterenko, P. Andersson, P.R. Haddad, J. Chromatogr. A 803 (1998) 279.
[9] H. Rohwer, N. Rheeder, E. Hosten, Anal. Chim. Acta 341 (1997) 263.

[10] F. Strelow, T. VanDerWalt, Talanta 26 (1979) 537.

[11] S. Sadeghi, D. Mohammadzadeh, Y. Yamini, Anal. Bioanal. Chem. 375 (2003) 698–702.

[12] G. Deng, G.E. Collins, J. Chromatogr. A 989 (2003) 311.

[13] D.C. MacLaren, M.A. White, J. Chem. Educ. 80 (2003) 623.

[14] G.E. Collins, Q. Lu, Anal. Chim. Acta 436 (2001) 181–189.

[15] C. Liu, J. Zachara, O. Qafoku, P. McKinley, S. Heald, Z. Wang, Geochim. Cosmochim. Acta 68 (2004) 4519.

[16] T. Fanghänel, V. Neck, Pure Appl. Chem. 74 (10) (2002) 1895–1907.