

Raman spectroscopy of selected arsenates—implications for soil remediation

Ray L. Frost^{a,*}, Theo Klopogge^a, Matthew L. Weier^a, Wayne N. Martens^a,
Z. Ding^a, Howell G.H. Edwards^b

^a Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, Qld. 4001, Australia

^b Department of Chemistry and Forensic Sciences, University of Bradford, Bradford, UK

Received 20 June 2002; accepted 15 August 2002

Abstract

The contamination of soils with heavy metals such as As, Cr and Cu is of great importance; the remediation of such soils even more so. Arsenic compounds are prevalent in soils either through leaching of mine tailings, the use of Cu/Cr/As as a wood preservative or through the use of arsenic in cattle dips. The arsenic compounds in soils and leachates can be highly reactive and mobile, resulting in the formation of metal arsenate compounds. Of these compounds, one such set of minerals that can be formed is the vivianite arsenate minerals. Raman spectroscopy has been used to characterise the vivianite arsenates and to identify arsenic contaminants in a soil.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Soil contamination; Arsenate; Soil remediation; Köttigite; Vivianite; Raman spectroscopy

1. Introduction

The presence of arsenic in soils is a widespread and common phenomenon [1–3]. The arsenate may have originated from old mine sites [4–7]. The arsenate in the soils is commonly mobile and can contaminate adjacent areas either through ground

water or other mechanisms such as through plant growth [3,8–10]. Arsenates in soils may originate from old munition dumps and from munition wastes such as from ‘Mustard gas’ [11,12]. Arsenates can form in soils through the leaching of old mine sites [13–16]. The effect of contamination of soils by arsenates can lead to phytotoxicity [6,17,18]. Arsenic compounds in conjunction with copper and chromium have been used extensively as a biocide to prevent borer attack in timber. This also is a cause of contamination of soils [19–21]. In Australia, arsenic compounds of an inorganic

* Corresponding author. Tel.: +61-7-3864-2407; fax: +61-7-3864-1508.

E-mail address: r.frost@qut.edu.au (R.L. Frost).

nature were used as the principal chemical ingredient in cattle dips [5,22,23]. The pH of the soil and post-contaminant treatment such as with lime or fertilisers containing phosphate can affect the speciation of the arsenic compounds [24,25]. No matter what the origin of the arsenic/arsenates in the soils, the identification of its presence is imperative. In this research, we present the Raman spectra of selected arsenate minerals and identify their presence in a contaminated soil.

The most likely minerals to be formed in soil contaminations are the minerals based upon the vivianite structure. The vivianite group of minerals consists of two groupings based upon the anion in the structure namely, phosphate or arsenate. The minerals are of interest because of the possibility of formation in environmental situations such as in the coatings of water pipes and in soils from peat bogs, morasses and sediments [26]. It is possible that the minerals can be formed from aqueous solutions from ground waters and precipitated from solutions in soils. If ground waters are high in both Mg^{2+} and Fe^{2+} then it is possible that both the minerals of the vivianite group such as baricite and bobierrite may form, particularly when phosphate fertilisers have been used in the surrounding farmlands. In fact, these minerals have been found in sediments in New Zealand [27]. The minerals of the vivianite group are of the general formula $\text{A}_3^{2+}(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$ where A^{2+} may be Co, Fe, Mg, Ni, Zn and X is As or P. Isomorphous substitution in this group occurs readily and combinations of the cations may be observed. The vivianite minerals are all monoclinic and point groups $2/m$ [27]. The minerals may be divided into two groups according to the oxyanion being either arsenate or phosphate [28]. The phosphates in this mineral group are aruptite ($\text{Ni}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), vivianite ($\text{Fe}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), baricite ($(\text{Mg},\text{Fe}^{2+})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and bobierrite ($\text{Mg}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$). The arsenates in this group are annabergite ($\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), erythrite ($\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), hörnesite ($\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), köttigite ($\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) (also written as koettigite) and parasymplectite ($\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$). Annabergite can form a continuous series with erythrite, which can also form a continuous series with hörnesite.

2. Experimental

2.1. Minerals

Synthetic vivianite arsenates of Zn, Fe, Co and Ni were prepared by the slow addition of the 3.5×10^{-3} M metal sulphate solution to a very dilute 5.0×10^{-3} M sodium arsenate solution using a peristaltic pump at 70 °C. The hydrated cationic arsenates precipitated from the solution and were filtered and dried. The crystals were hydrothermally treated and were grown by Ostwald ripening at 70 °C for 14 days. Samples were analysed for phase purity by X-ray diffraction and for chemical composition by ICP-AES and also by electron probe analyses. Because hörnesite and köttigite were not obtained of sufficient known cationic purity, the spectroscopic analyses used in this work are based upon the synthesised minerals.

A contaminated soil was obtained for analysis from an old cattle dip site in South East Queensland. The annabergite originated from the 132 North Deposit, Widgiemooltha District of Western Australia. The erythrite (large scarlet cobalt crystals) originated from Mt. Cobalt Queensland, Australia. Köttigite from the Ojuela Mine, Mapini, Durango, Mexico was obtained from the South Australian museum (sample number G21998). The minerals were analysed for phase purity by powder X-ray diffraction methods and for chemical composition using SEM EDAX techniques.

2.2. Raman microprobe spectroscopy

The crystals of the vivianite minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10 and 50 $\times$ objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge coupled device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio in the spectra. Spectra

were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, UK).

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss–Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and discussion

The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion (ν_1) is observed at 810 cm^{-1} and coincides with the position of the asymmetric stretching mode (ν_3). The symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the out-of-plane bending modes (ν_4) is observed at 398 cm^{-1} . Of all the tetrahedral oxyanions spectra, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. Farmer lists a number of infrared spectra of arsenates including annabergite, erythrite, symplectite and köttigite [29]. The effect of the arsenate ion in a crystal will be to remove the degeneracy and allow splitting of the bands according to factor group analysis. The ν_1 and ν_3 bands of annabergite were observed at 832 and 795 cm^{-1} . The bending modes were found at 510 , 460 and 427 cm^{-1} for annabergite. No ν_2 bands were shown. This is no doubt related to the fact the bands are found below 400 cm^{-1} , which makes the measurement by infrared spectroscopy diffi-

cult. Two OH stretching vibrations were observed at 3430 and 3160 cm^{-1} for annabergite. A number of bands were listed which were unassigned.

The symmetric stretching vibration of the phosphate anion (ν_1) is observed at 938 cm^{-1} , the asymmetric stretching mode (ν_3) at 1018 cm^{-1} . The ν_2 mode is observed at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} . Farmer lists a number of infrared spectra of phosphates including vivianite [29]. The symmetric stretching mode was not listed but the antisymmetric mode was found at 990 and 1040 cm^{-1} . Bands at 890 and 872 cm^{-1} were not assigned. Bands for the ν_4 mode were observed at 475 , 560 and 590 cm^{-1} . Griffith reported the Raman spectra of vivianite [30].

Experimental work has shown that the arsenates of the vivianite structure are most readily formed. Whilst the mineral formation is controlled by pH, the minerals are easily formed at room temperature. The laboratory work shows that the minerals can readily form in soils. The starting material is simply the arsenate anion, which is soluble in dilute solutions. Upon reaction with metal cations, insoluble arsenates may form. Of course minerals such as arsenites may also form. Minerals other than those of the vivianite arsenates may also form, for example, talmessite. Further at high pH, the basic metallic arsenates of the adelite group may form. In acid soils, it is more likely that vivianite minerals are formed.

The Raman spectra of the AsO stretching region of arsenates of Ni, Co, Fe, Mg are shown in Fig. 1 and also the Raman spectrum of vivianite (the common phosphate of iron spectrum (e)). The figure also shows the Raman spectrum of a contaminated soil (spectrum (f)). For each mineral except köttigite, two intense bands are observed. The position of these bands appears to vary depending on the cation. The bands are observed at 854 and 800 cm^{-1} for annabergite. The band observed at 941 cm^{-1} for the natural annabergite may be assigned to some phosphate isomorphic substitution. Raman spectral studies of the vivianite phosphates show that there is a band at 951 cm^{-1} for vivianite. The bands are observed at 852 and 792 cm^{-1} for erythrite and at 875 and 807 cm^{-1} for hörnesite. Köttigite Raman spectrum is the exception and it is suggested that the band

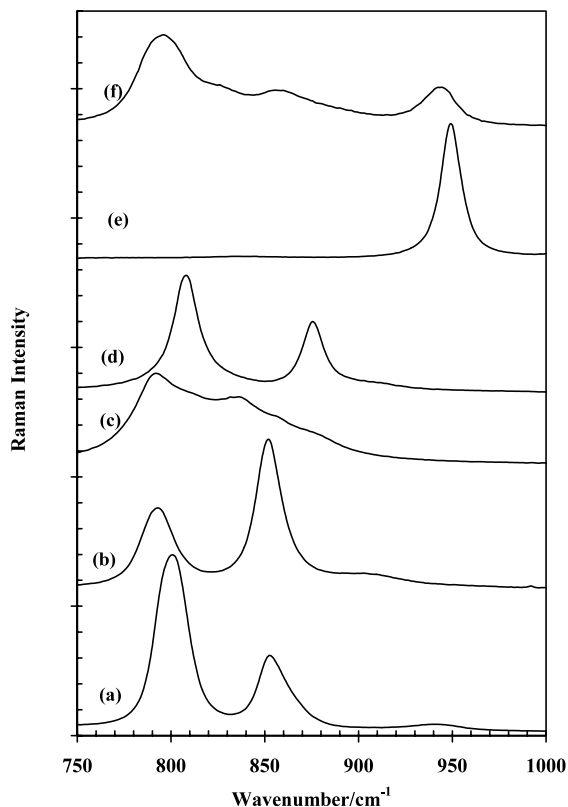


Fig. 1. Raman spectra of the AsO stretching region of (a) annabergite; (b) erythrite; (c) köttigite; (d) hörnesite; (e) vivianite and (f) soil sample.

profile is made up of two overlapping sets of two bands. These are 790 and 835 cm^{-1} and 811 and 868 cm^{-1} . Both these bands are assigned to the ν_1 symmetric stretching modes of A_1'' symmetry. Griffith reported Raman bands for a synthetic annabergite at 880 , 859 , 820 and 797 cm^{-1} . The low intensity band observed around 902 cm^{-1} is assigned to the E_{1g} mode.

In the Raman spectrum of vivianite a single intense band is observed at 949 cm^{-1} with low intensity bands observed at 1081 , 1050 and 1015 cm^{-1} . The 949 cm^{-1} band is assigned to the Raman active PO stretching vibration. The position of this band is in excellent agreement with the previously published result [31]. The bands at 1081 , 1050 and 1015 cm^{-1} are assigned to the phosphate PO antisymmetric stretching vibrations. The 1081 cm^{-1} band is very low in intensity. Pirou

and Poullen found bands at 1053 and 1018 cm^{-1} and are in agreement with our results. We did not observe the band at 990 cm^{-1} . The phosphate anion in an aqueous solution shows a single antisymmetric band at 1017 cm^{-1} . In this work three bands are observed, which suggests that the phosphate ion is reduced in symmetry from T_d to C_{3v} or less to C_{2v} . Previously published infrared data reported by Farmer gave bands at 1040 and 990 cm^{-1} , which are different from the results reported here. One possibility is that the data is correct the identification of the mineral incorrect.

Analysis of the Raman spectrum of the contaminated soil (spectrum (f)) suggests that both the arsenate and phosphate anions are present in the sample. The position of the phosphate band is slightly less than that of vivianite. The arsenate spectrum more closely resembles that of köttigite. Köttigite forms continuous series with both hörnesite and parasymphesite. In other words, the soil contamination is of a mixed cationic arsenate species, which is principally based upon iron. It is not known whether the phosphate is isomorphically substituting into the vivianite structure. Thus the Raman spectrum may be simply the addition of the arsenate and phosphate spectra. Alternatively the spectrum may be of a single mineral. Other techniques such as X-ray diffraction may be required to solve this problem.

The low wavenumber region of the vivianite arsenates between 100 and 500 cm^{-1} is shown in Fig. 2. The low wavenumber region is complex and it is difficult to separate the Raman bands according to their symmetry. The spectrum of the low wavenumber region may be divided into three separate regions: (a) 400 – 500 cm^{-1} , (b) 250 – 400 cm^{-1} and (c) 100 – 250 cm^{-1} . It is proposed that these three regions define the (a) ν_4 modes, (b) ν_2 modes and (c) AsO bending and lattice modes. The ν_2 bending vibration should be common to all three spectra and should be intense. The most intense bands occur in two regions, (a) around 450 cm^{-1} and around 225 cm^{-1} . The two most intense bands for annabergite are observed at 203 and 225 cm^{-1} . It is noted that for the synthetic annabergite, Raman bands are observed at almost identical positions. The two most intense bands for erythrite are found at 209 and 249 cm^{-1} .

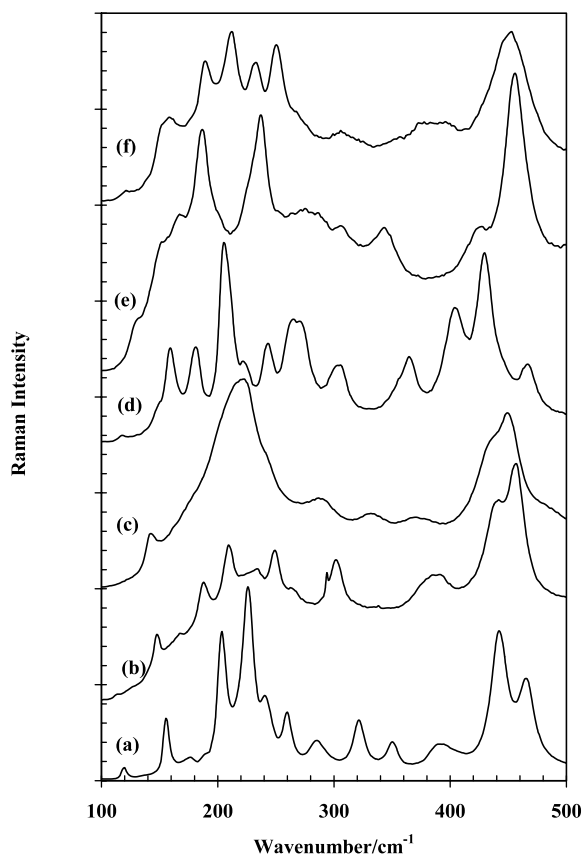


Fig. 2. Raman spectra of the low wavenumber region of (a) annabergite; (b) erythrite; (c) köttigite; (d) hörnesite; (e) vivianite and (f) soil sample.

The complex overlapping pattern of bands in the AsO stretching region is also reflected in the 223 cm^{-1} region of köttigite. This region may be deconvoluted into bands at 249 , 220 and 194 cm^{-1} . For the synthetic hörnesite, a single intense band is observed at 206 cm^{-1} . Bands in these positions have not been reported for the infrared spectra. Fundamentally, the bands are below the normal operation limits of mid-IR spectrometers. These bands are assigned to the OAsO bending modes.

The second most intense region in the Raman spectra is around the 450 cm^{-1} region. For both the natural and synthetic annabergites, two bands are observed at 466 and 442 cm^{-1} and for erythrite bands are observed at 457 and 439 cm^{-1} . For köttigite, bands are observed at 451

and 432 cm^{-1} . These bands are attributed to the ν_4 bending modes. The positions of these bands are observed at slightly lower wavenumbers for hörnesite and are found at 429 and 403 cm^{-1} . Farmer reported the infrared spectra of annabergite and erythrite. He gave infrared band positions of 510 , 460 and 427 cm^{-1} for annabergite and at 490 , 452 and 428 cm^{-1} for erythrite. The latter two bands for these two minerals are in excellent agreement with the Raman bands reported in this work. Griffith reported the ν_4 modes in the Raman spectra at 452 and 438 cm^{-1} .

One of the strong advantages of Raman spectroscopy is the ability to obtain spectral data below 400 cm^{-1} . The difficulty is the attribution of the multiple bands found in this region. In aqueous solutions of the phosphate ion, the band observed at 420 cm^{-1} is assigned to the ν_2 bending mode. For vivianite, two bands are observed at 423 and 456 cm^{-1} , with the latter being the most intense. The observation of two bands for the OPO bending region suggests the loss of degeneracy of the bending mode. The only Raman data for comparison is that reported by Griffith, who suggested the bending mode was at 316 cm^{-1} [30]. However, this seems to be an error. Farmer also did not report the bending mode. For aqueous systems the ν_4 mode of phosphate is observed at 567 cm^{-1} . For vivianite, four bands are observed at 584 , 569 , 545 and 530 cm^{-1} . The 569 cm^{-1} band is intense and sharp. These bands are assigned to the ν_4 modes of vivianite. The spectral data reported by Griffith is at variance with these results [30]. Farmer reported infrared bands at 590 , 560 and 475 cm^{-1} [29]. The difficulty in the study of this spectral region is a combination of the complexity of the overlap and the number of bands. In the Raman spectrum, for vivianite two intense bands are observed at 236 and 186 cm^{-1} . One possibility is that these bands are attributable to FeO stretching vibrations.

The Raman spectrum of the low wavenumber region of the soil sample shows little resemblance to that of any of the arsenate samples or to the phosphate vivianite spectrum. A broad band is observed at 454 cm^{-1} , which may correspond to the band at 457 cm^{-1} for vivianite. The Raman

spectrum in the 150–250 cm⁻¹ region more closely resembles that of hörnesite.

4. Conclusions

Importantly Raman spectroscopy enables the identification of bands attributable to the mineral arsenate and phosphate units. Each mineral possesses its own characteristic Raman spectrum enabling the ready rapid identification of the mineral. Raman spectroscopy is a very powerful tool for the analysis of arsenate compounds in contaminated soils. The significance of the work rests with the rapid identification of possible arsenate contaminants in soils [6,7,32,33]. Further the identification of the minerals allows for possible remediation of the soils [12,34].

Acknowledgements

The financial and infra-structure support of the Queensland University of Technology Inorganic Materials Research Program is gratefully acknowledged. The Australian research Council (ARC) is thanked for funding.

References

- [1] W.W. Wenzel, A. Brandstetter, H. Wutte, E. Lombi, T. Prohaska, G. Stinger, D.C. Adriano, *J. Plant Nutr. Soil Sci.* 165 (2002) 221.
- [2] P.S. Yarlagadda, M.R. Matsumoto, J.E. Vanbenschoten, A. Kathuria, *J. Environ. Eng. (NY)* 121 (1995) 276.
- [3] P.W. Abrahams, I. Thornton, *Agric. Ecosyst. Environ.* 48 (1994) 125.
- [4] E.H. Amonoo-Neizer, D. Nyamah, S.B. Bakiamoh, *Water Air Soil Pollut.* 91 (1996) 363.
- [5] P.M. Ashley, B.G. Lottermoser, *Aust. J. Earth Sci.* 46 (1999) 861.
- [6] J. Bech, C. Poschenrieder, M. Llugany, J. Barcelo, P. Tume, F.J. Tobias, J.L. Barranzuela, E.R. Vasquez, *Sci. Total Environ.* 203 (1997) 83.
- [7] M. Chen, L.Q. Ma, C.G. Hoogeweg, W.G. Harris, *Environ. Forensics* 2 (2001) 117.
- [8] D.K. Bhumbra, R.F. Keefer, *Adv. Environ. Sci. Technol.* 26 (1994) 51.
- [9] A. Brandstetter, E. Lombi, W.W. Wenzel, D.C. Adriano, *Environ. Sci. Pollut. Control Ser.* 23 (2000) 715.
- [10] J. Christova, C. Stanchev, K. Rekalov, *Dokl. Bulg. Akad. Nauk.* 46 (1993) 81.
- [11] Beletskaya, Bilger, Boronin, Bunnett, Costantino, Cullen, Dominas, Goessler, Haiduc, Maeda, Martens, NATO ASI Series, Series I: Disarmament Technologies 19, 1998, pp. 177.
- [12] F. Juillot, P. Ildefonse, G. Morin, G. Calas, A.M.D. Kersabiec, M. Benedetti, *Appl. Geochem.* 14 (1999) 1031.
- [13] T.R. Ruede, H. Puchelt, *Soil Environ.* 5 (1995) 413.
- [14] R. Pongratz, *Sci. Total Environ.* 224 (1998) 133.
- [15] M. Navarro, M. Sanchez, H. Lopez, M.C. Lopez, *Bull. Environ. Contam. Toxicol.* 50 (1993) 356.
- [16] G. Maini, A.K. Sharman, C.J. Knowles, G. Sunderland, S.A. Jackman, *J. Chem. Technol. Biotechnol.* 75 (2000) 657.
- [17] M.B. McBride, C.E. Martinez, *Environ. Sci. Technol.* 34 (2000) 4386.
- [18] H. Helgesen, E.H. Larsen, *Analyst (Cambridge UK)* 123 (1998) 791.
- [19] J. Rajander, L. Harju, J.O. Lill, K.E. Saarela, A. Lindroos, S.J. Heselius, *Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. Atoms* 150 (1999) 510.
- [20] D.E. Stilwell, K.D. Gorny, *Bull. Environ. Contam. Toxicol.* 58 (1997) 22.
- [21] M.F. Azizian, K. Osathaphan, P.O. Nelson, Preprints of extended abstracts presented at the ACS national meeting, American Chemical Society, Division of Environmental Chemistry 40, 2000, 16.
- [22] Q. Zhou, Z. Gao, *J. Environ. Sci. (Chin.)* 6 (1994) 330.
- [23] R.G. McLaren, R. Naidu, J. Smith, K.G. Tiller, *J. Environ. Qual.* 27 (1998) 348.
- [24] M. Panssar-Kallio, P.K.G. Manninen, *Sci. Total Environ.* 204 (1997) 193.
- [25] F.J. Peryea, R. Kammereck, *Water Air Soil Pollut.* 93 (1997) 243.
- [26] G.S. Henderson, P.M. Black, K.A. Rodgers, P.C. Rankin, *New Zealand J. Geol. Geophys.* 27 (1984) 367.
- [27] B.R. Anthony, J.W. Bideaux, K.W. Bladh, M.C. Nichols, *Handbook of Mineralogy, volume IV Arsenates, Phosphates and Vanadates*, vol. 4, Mineral Data Publishing, Tucson, AZ, USA, 2000, p. 2000.
- [28] C.W. Wolfe, *Am. Mineral.* 25 (1940) 738.
- [29] V.C. Farmer, *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*, 1974.
- [30] W.P. Griffith, *J. Chem. Soc., A* (1970) 286.
- [31] B. Piriou, J.F. Poullen, *Bull. Mineral.* 110 (1987) 697.
- [32] M.B. Alam, M.A. Sattar, *Water Sci. Technol.* 42 (2000) 185.
- [33] A. Davis, M.V. Ruby, M. Bloom, R. Schoof, G. Freeman, P.D. Bergstrom, *Environ. Sci. Technol.* 30 (1996) 392.
- [34] E. Lombi, W.W. Wenzel, D.C. Adriano, *Environ. Sci. Pollut. Control Ser.* 23 (2000) 739.