

FTIR Spectra Analysis of Sediment Influenced by Acid Mine Drainage

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Abstract. The contamination of aquatic and terrestrial ecosystems with heavy metals and other mining chemicals have been major environmental problems in many mining areas of the world. Industrial wastes, geochemical structure and metals mining form a potential source of metal contaminants in the aquatic environment especially in sediment. In Slovak Republic there are some localities with existing acid mine drainage (AMD) generation conditions. The most critical values were observed in the abandoned deposit Smolnik. Waters from the earth surface penetrated the mine and they are enriched with metals and their pH values decreased. Increasing of pH after their mixing with surface water has negative influence on accumulation of pollutants in sediment.

The aim of this paper is to investigate the use of Fourier transform infrared (FTIR) transmittance spectroscopy for identification of changes of functions group in the sediment composition influenced by acid mine drainage. Chemical parameters of sediment quality were studied also by X-ray fluorescence spectrometry (XRF).

Keywords: acid mine drainage, sediment, infrared spectroscopy, X-ray fluorescence spectrometry.

Conference topic: Environmental protection.

Introduction

Sediments are principal carriers of the trace elements in the hydrosphere. Sediment particles are made up of materials derived from rock, soil, biological and anthropogenic inputs. The basic structural unit of inorganic sediment is silicate and aluminosilicate. Major components of sediments include clay, quartz, feldspars, various silicate minerals, gibbsite and calcium carbonate. They have been classified in a variety of ways according to different criteria such as their source, particle size and their composition (Sivakumar *et al.* 2012).

Due to spatial and temporal variations in water and sediment chemistry, a monitoring program that provides a representative and reliable estimation of the quality of surface waters and bottom sediments has become an important necessity (Angelovicova, Fazekasova 2013). Pollution of the natural environment by heavy metals is a universal problem because of their undegradability. Transmission spectroscopy is the oldest and most commonly used method for identifying either organic or inorganic chemicals providing specific information on molecular structure, chemical bonding and molecular environment. It can be applied to study solids, liquids or gaseous samples being a powerful tool for qualitative and quantitative studies. From the IR absorption band or locations of the different peaks, the minerals were identified with the available literature. In addition to the band position, sharpness or diffuseness of bands helpful in the identification of mineral components. The IR study on sediment samples was highly useful in identifying the various minerals in sediment. This method was non-destructive and can be used in the identification of mineralogical composition. These results confirmed that applied technique is relatively quicker and more reliable in mineral analysis (Simonescu 2012). The IR study on sediment samples was highly used. The most critical values were observed also in the abandoned deposit Smolnik (Petrilakova, Balintova 2011). Overflowed mine Smolnik produces AMD with high metal concentrations and low value of the pH (about 3–4) as a result of chemical oxidation of sulphides and other chemical processes. This was the reason for starting a systematic monitoring of geochemical development in acid mine drainage in order to prepare a prognosis in terms of environmental risk and use of these sediment as an atypical source of a wide range of elements (Slesarova *et al.* 2007). The paper deals with the study of sediment quality from Smolnik Creek, East of Slovakia using of XRF and FTIR analyses.

Study area and sampling sites localizations

The stratiform deposit Smolnik belongs to the historically best-known and richest Cu – Fe ore deposits in Slovakia. In 1990 the mining activity at the locality was stopped. The mine was flooded till 1994. In 1994 an ecological collapse occurred, which caused the death of fish and the negative influence on the environment. The mine-system represents a partly opened geochemical system into which rain and surface water drain (Spaldon *et al.* 2006; Luptakova *et al.* 2007). The analysis of water in the deserted mine and in the broader area surrounding this mine was made after the ecological accident in the Smolnik creek in 1995. Waters from the earth surface penetrated the mine and they were

enriched with metals and their pH values decreased (Sottnik *et al.* 2002). Acidity is caused mainly by the oxidation of sulphide minerals. The Pech shaft receives the majority of waters draining from the flooded Smolnik mine area and discharges them in the form of acid mine drainage (pH = 3–4, Fe 500–400 mg/l; Cu 3–1 mg/l; Zn 13–8 mg/l and Al 110–70 mg/l). This water acidifies and contaminates the Smolnik creek water which transports pollution into the Hnilec River catchment (Luptakova *et al.* 2008).

For monitoring the current status of sediment quality parameters, four sampling and AMD collection localities were selected at Smolnik creek directly from the Pech shaft. Monitoring was carried out in the 2006–2016 period. Sediment sampling localities (Fig. 1) are located 48° (south latitude) and 20° meridians (east longitude). Two localities were in the upper part of the Smolnik creek without contamination by acid mine waters from the Pech shaft (1 – outside the Smolnik village, 2 – small bridge – crossing to the shaft Pech and another two sampling localities were located under the shaft (4 – 200 m under the shaft Pech, 5 – inflow to the Hnilec river). The outflow of AMD from Pech shaft (Smolnik mine) is number 3.

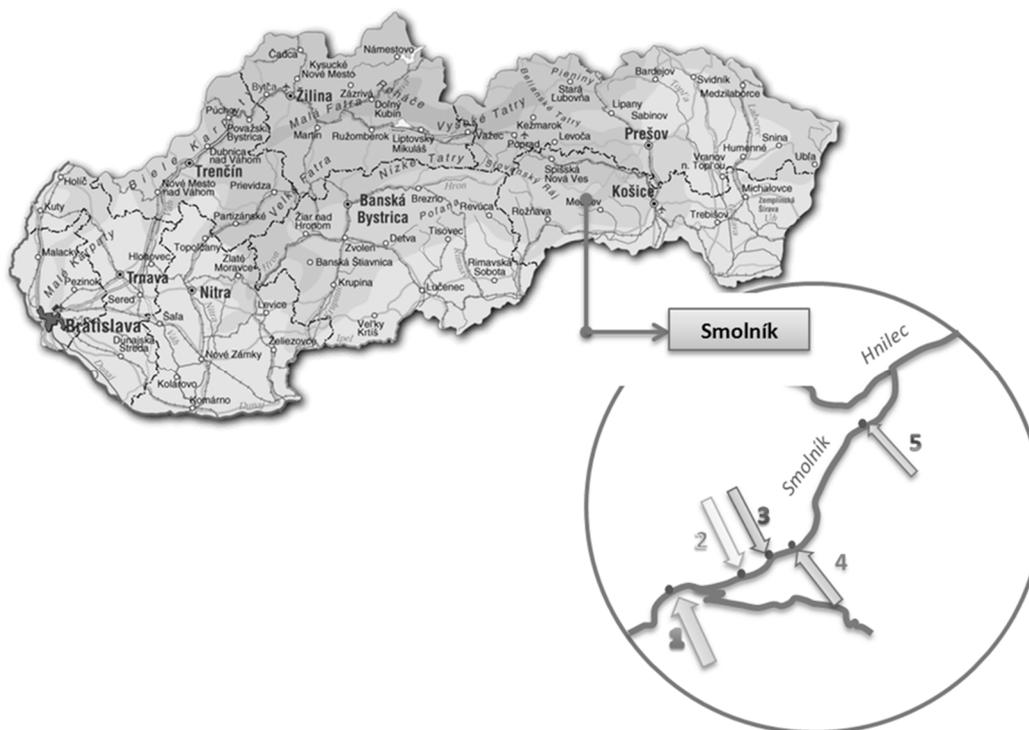


Fig. 1. Sampling sites of sediment in the selected locality

Materials and methods

The sediment was dried, homogenized and sieved below 0,063 mm. Chemical analyses were performed by the XRF method using by SPECTRO iQ II (Ametek, Germany). Results of chemical analyses of the sediment were compared with the limited values according to the Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields. For infra-red spectroscopy in this study, was Alpha FT-IR Spectrometer, BRUKER OPTICS. To provide a good characterization of mineral by infrared spectroscopy, the spectrum should be recorded in the range of 4000–600 cm^{-1} . Such coverage of range ensures that most of the useful vibrations active in the infrared will be included. The instrument scans the spectra 24 times in 1 minute and resolution is 5 cm^{-1} .

Result and discussion

The results of chemical analysis of sediment samples in the East of Slovakia are presented in Table 1. The results were compared with the limit values according to the Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields. The results showed that rated sediments did not meet the limit values for arsenic, cadmium and concentrations of lead was also exceeded.

An increase in the concentration of Fe, Cu and Zn in samples S4 and S5 of sediments compared to sediment samples S1 and S2 can be connected with their precipitation in accordance with the results presented by (Matlock *et al.* 2002), iron precipitated at pH 3.5–4, 5; copper at pH 5.5–6.5; Zn at pH 5.5–7.0; Al at 4.5–5.5 which were the main reasons for the researching the impact of flow on the pH of surface waters.

Table 1. Concentration of heavy metals in sediment from sample sites of Smolnik Creek

No	Year	SO ₄ ²⁻	Ca	Mg	Fe	Mn	Al	Cu	Zn	As	Cd	Pb	
		[%]						[mg/kg]					
S1	2006	<0.01	0.45	0.93	3.96	0.108	7.02	176	171	50	<0.5	50	
	2007	<0.01	0.30	0.74	3.88	0.044	7.14	103	123	35	<0.5	39	
	2008 A	<0.01	0.26	0.70	3.49	0.062	6.88	114	140	31	<0.5	44	
	2008B	<0.01	0.30	0.73	4.01	0.116	7.67	128	157	52	<0.5	43	
	2009	<0.01	0.21	0.85	4.57	0.09	7.68	111	143	47	<0.5	35	
	2011	0.07	0.36	0.81	4.92	0.12	8.08	148	179	52	<0.5	43	
	2012	0.06	0.21	0.82	4.64	0.1	8.14	190	174	56	<0.5	60	
	2013	0.07	0.27	0.84	4.75	0.11	8.02	199	184	66	<0.5	61	
	2014	0.02	0.19	0.75	3.93	0.08	6.86	78	113	27	<0.5	32	
	2015	0.04	0.35	0.68	3.4	0.07	6.32	78	122	29	<0.5	28	
2016	0.03	0.31	0.75	4.08	0.11	7.5	118	135	41	<0.5	40		
S2	2006	1.00	0.21	0.81	6.76	0.040	7.32	234	183	84	<0.5	82	
	2007	0.4	0.22	0.73	5.70	0.051	6.76	282	186	88	<0.5	100	
	2008 A	0.10	0.37	0.70	4.13	0.073	6.43	252	196	64	<0.5	89	
	2008B	0.75	0.14	0.72	7.27	0.051	7.21	237	180	104	<0.5	93	
	2009	0.40	0.16	0.72	4.63	0.04	6.63	196	131	65	<0.5	59	
	2011	0.12	0.32	0.79	5.83	0.08	6.77	467	273	81	<0.5	147	
	2012	0.34	0.21	0.78	6.25	0.06	7.32	368	200	111	<0.5	145	
	2013	0.38	0.15	0.73	4.73	0.04	6.75	197	131	56	<0.5	76	
	2014	0.35	1.9	<0.05	0.66	4.03	0.04	6.31	135	87	44	<0.5	<0.5
	2015	0.12	0.26	0.66	4.49	0.06	6.26	423	190	83	<0.5	122	
2016	0.23	0.19	0.69	4.67	0.05	6.99	209	150	66	<0.5	74		
S3	2006	19.08	8.73	1.38	23.6	0.096	2.52	448	313	909	<0.5	135	
	2007	14.01	0.09	0.21	39.7	0.012	0.46	215	58	1465	<0.5	38	
	2008 A	8.80	0.03	0.72	34.6	0.022	4.01	689	150	2206	<0.5	1557	
	2008B	7.83	0.07	0.86	26.6	0.024	4.65	663	168	2439	<0.5	2731	
	2009	14.12	0.10	0.21	37.4	0.01	0.74	143	45	1500	<0.5	48	
	2011	10.9	0.12	0.44	33.0	0.02	2.37	756	128	1975	<0.5	1081	
	2012	9.51	0.06	0.64	32.8	<0.01	2.91	603	142	2358	<0.5	225	
	2013	11.7	0.08	0.17	38.6	0.01	1.42	495	81	2307	<0.5	215	
	2014	11.7	0.05	0.2	38.5	0.02	1.49	432	56	2603	7.0	398	
	2015	12.8	0.09	0.17	38.8	<0.01	1.37	380	52	3617	<0.5	366	
2016	11.3	0.09	0.13	39.9	<0.01	1.77	433	57	3472	<0.5	265		
S4	2006	2.42	0.19	0.64	13.8	0.051	6.09	445	172	154	<0.5	172	
	2007	0.96	0.40	0.83	12.3	0.084	6.46	903	328	253	<0.5	282	
	2008 A	0.30	0.57	0.78	4.97	0.067	6.16	365	214	201	<0.5	328	
	2008B	1.21	0.19	0.80	8.90	0.048	6.84	295	172	161	<0.5	198	
	2009	0.30	0.21	0.72	5.07	0.05	6.91	281	165	68	<0.5	101	
	2011	0.36	0.27	0.80	5.42	0.06	6.54	363	191	92	<0.5	110	
	2012	1.16	0.27	0.89	11.6	0.04	6.63	670	276	245	<0.5	225	
	2013	1.01	0.19	0.68	8.81	0.07	6.39	352	169	122	<0.5	133	
	2014	0.1	<0.05	0.66	3.63	0.04	6.59	113	90	46	<0.5	52	
	2015	0.27	0.26	0.61	4.95	0.07	5.67	254	191	80	<0.5	108	
2016	0.09	0.14	0.7	3.96	0.04	7.03	122	107	49	<0.5	49		
S5	2006	0.38	0.14	0.66	7.84	0.044	6.55	506	250	97	<0.5	111	
	2007	0.29	0.25	0.83	8.82	0.057	6.29	661	320	146	<0.5	159	
	2008 A	0.27	0.32	0.79	6.24	0.068	6.39	404	193	135	<0.5	176	
	2008B	-	0.17	0.44	13.2	0.045	7.26	527	192	83	<0.5	106	
	2009	4.90	0.08	0.27	31.7	0.03	2.62	836	200	84	<0.5	15	
	2011	0.32	0.32	0.79	5.73	0.07	6.71	427	242	93	<0.5	117	
	2012	0.21	0.28	0.84	6.85	0.05	6.55	585	323	102	<0.5	119	
	2013	0.19	0.27	0.66	5.58	0.06	6.12	482	225	91	<0.5	112	
	2014	0.09	0.13	0.71	4.42	0.07	6.98	241	195	51	<0.5	68	
	2015	0.34	0.3	0.74	7.43	0.09	6.8	523	263	96	<0.5	126	
2016	0.33	0.19	0.71	5.57	0.05	6.77	406	229	90	<0.5	117		
Limits		-	-	-	-	-	-	1000	2500	20	10	750	

Infrared spectra of the selected sediments are shown in Figure 2.

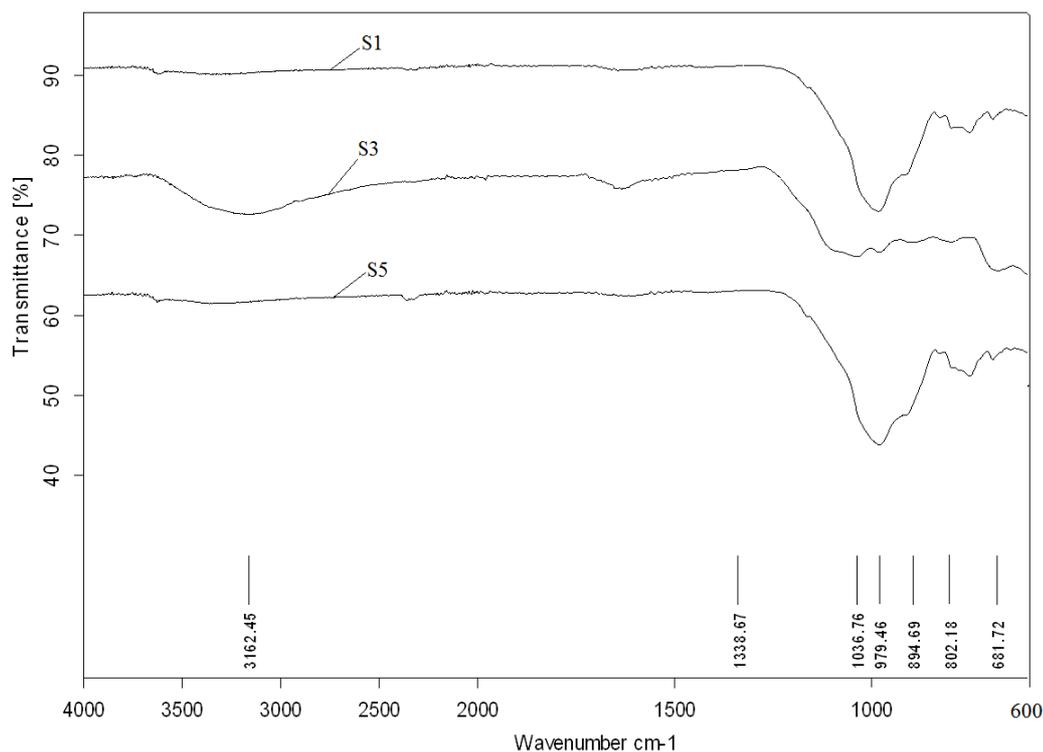


Fig. 2. Sampling sites S1, S3, S5 of sediment in the selected locality

The absorption frequencies of the peaks in the spectra of sites S1, S3, S5 in wave number unit (cm^{-1}) and their intensity are reported in Table 2.

Table 2. Observed IR absorption frequencies of sediment samples and their intensity of Smolnik Creek

No.	Observed IR absorption frequencies (cm^{-1})	Intensity
S1	3625	0,01
	3365	0,028
	2356	0,015
	2030	0,009
	1642	0,013
	979	0,292
	749	0,061
	692	0,020
S3	3162	0,119
	1338	0,003
	1036	0,143
	979	0,014
	895	0,033
	802	0,010
	682	0,033
	599	0,023
S5	3625	0,01
	3365	0,028
	2356	0,015
	2030	0,009
	1642	0,013
	979	0,292
	749	0,061
	692	0,020

The infrared spectrum of sample S3 confirmed the presence of hydroxysulphate, which is dominated by a broad, OH-stretching band centred at 3100 cm^{-1} . Another prominent absorption feature related to H_2O deformation is expressed at 1634 cm^{-1} . Intense bands at 1124 , and 1038 cm^{-1} reflect a strong splitting of the $\nu_3(\text{SO}_4)$ fundamental due to the formation of a bidentate bridging complex between SO_4 and Fe. Vibrations at 753 and 424 cm^{-1} are attributed to Fe-O stretch; however, the assignment of the former is tentative because similar bands in iron oxyhydroxides usually occur at lower frequencies. A broad absorption shoulder in the 800 to 880 cm^{-1} range is apparent in some specimens and is related to OH deformation ($\nu(\text{OH})$) (Pacakova *et al.* 2000). These results are in accordance with the work of (Pallova *et al.* 2010) who determined the presence of $\text{Fe}_{16}\text{O}_{16}(\text{SO}_4)_3(\text{OH})_{10}\cdot 10\text{H}_2\text{O}$ by XRD method in sediment from AMD at Smolnik.

FTIR spectra of all homogenized sediment samples (S1 and S5) showed similar features. Based on the data from (Guihua *et al.* 1998) it can be said that the main part of compounds are silicates including quartz (982 , 825 , 753 , 695 , 518 cm^{-1}), but hydroxides (3600 – 3650 cm^{-1} ; 1652 cm^{-1}) are present, too.

Conclusions

Analysis of sediments provides environmentally significant information. Their chemical characterization is needed to understand the natural and anthropogenic influence on the bodies of water. In the present study, sediment collected from Smolnik creek on east of Slovakia is subjected to mineral analysis using FTIR technique. The major minerals for its FTIR absorption peaks were hydroxisulphate, hydroxides and quartz. It was not confirmed an expected results of the bigger portion of hydroxides after in the sediment influenced by acid mine drainage (S4, S5). The performed analyses provide useful information about mineralogical composition of the sediments. This is a fundamental step gaining knowledge about constituent of minerals.

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