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**APPLICATION OF X-RAY MICROANALYTICAL METHODS TO MINING
RELATED ENVIRONMENTAL PROBLEMS**

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1. ABSTRACT

The combination of non-destructive X-ray microanalytical techniques is demonstrated on two mining related environmental problems in Hungary. The fate of the heavy metal pollution of the Tisza River and its tributaries due to mine tailings failure in the Romanian part of the river, as well as the possible leaching of uranium and other heavy metals from the recultivated uranium mine in Mecsek Mountains were studied. Microscopic grains containing heavy metals at elevated concentration are characteristic for both situations. Carefully selected microparticles were subjected to thorough investigations using various X-ray microanalytical techniques, i) electron probe X-ray microanalysis for major elemental composition, ii) microscopic X-ray fluorescence analysis for minor and trace elemental composition, iii) microscopic X-ray absorption near-edge structure spectroscopy for the chemical state of selected metals, and iv) microscopic X-ray diffraction for determination of the crystalline phases. The combination of the four techniques provides valuable complementary information to bulk chemical analysis of tailings and sediment material.

2. INTRODUCTION

Mining and mineral processing operations produce large amounts of waste which are deposited in waste dumps and tailings, containing fine-grained material. Several mine tailing dam failures around the world have affected the ecosystems along the floodplain and riverbed. Some of them had immediate effect and needed clean up operation to remove waste and polluted vegetation. Such dam failures normally involve huge volumes of contaminated effluents and are later discharged to river systems and can be transported for hundreds of kilometres. Often the environmental implications are not immediate as the toxic metals remain in the mineral, solid phase. During longer time scales these potentially detrimental metals can leach into the water but can also leach accidentally if some bacterial activity is important.

Trace and microanalysis techniques can be useful in the context of both acute environmental disasters and long-term releases of pollutants as a means of tracing pollution sources from the chemical fingerprint of such heterogeneous material.

An important mining and industrial area is located in the catchment area of the Tisza River that suffered several major accidents in year 2000. The two major tailings dam failures that occurred in January and March 2000 in NW Romania, contaminated the Sasar-Lapuș-Someș (Szamos) and Novaț-Vaser-Vișeu river systems, respectively. Since then, different stakeholders, the authorities and the research sector have carried out thousands of analyses to monitor the water quality. Sediment analysis, however, was only carried out almost exclusively on the Tisza River, but only occasionally or not at all on the small tributaries as the Szamos and Túr. These rivers are low-gradient and high-sinuosity with some flood-defence embankment in the urban sections.

The cyanide disaster (Baia Mare accident) occurred in January 2000 caused an acute environmental and ecological damage that has been widely discussed [1-3]. The transboundary nature of both accidents arise questions concerning environmental policy and international law [4]. The second pollution event caused by a mine tailings dam failure at Baia Borşa released heavy-metal containing sludge to the tributary of the Tisza River. The severe and chronic environmental consequences of that accident inspired an increasing number of scientific papers [5-8]. The studies use bulk analytical techniques for chemical characterisation of the water and sediment samples.

Uranium as a necessary raw material for the nuclear fuel cycle is usually extracted from uranium ore. There exists only one uranium ore deposit in Hungary that is located in the south of the country at the foot of the Mecsek Mountains at the western border of the city of Pécs. Before 1989, the uranium production was 500 - 550 tonnes per year from ores at grades of 0.1 % that was completely shipped to the Soviet Union. The production completely stopped in 1997. Since then, a project sponsored by the Hungarian Government started in order to decrease and eliminate the damages caused mostly by the waste ore tailings and mill tailings. The tailings from uranium recovery were deposited in ponds in an open area between the Tortyogó and Pellérd water bases, which are resources of drinking water of Pécs and the neighbouring villages [9]. Therefore the continuous monitoring of the U level of the water effluents is important both for chemical cleaning technology and public health. A good hydrogeochemical modelling of the migration of uranium and other heavy metals in groundwater would be very important concerning the public health effects related to the water base [10]. Mine tailings and waste rock piles are the main environmental contamination sources of the territory of the mine.

The sediment and tailings materials are highly inhomogeneous, microscopic grains having orders of magnitude higher heavy metal concentrations than the surrounding material are characteristic for both environmental problems. In order to obtain quantitative chemical information on sediments and suspended particulate matter, including concentration and speciation of pollutant heavy metals, the use of bulk analytical techniques and extended sample sets is mandatory. However, if the identification of specific samples and specific particle types characteristic for the pollution is possible, additional information on the chemical changes of the pollution-related elements can be obtained by analysis of individual particles. This information cannot be quantitative for the whole material, but gives insight to the fate of the particles/grains of anthropogenic origin. The present paper demonstrates a combination of non-destructive microanalytical methods providing detailed information on the trace composition, distribution and speciation of heavy metals in carefully selected single particles originating from mining activities.

3. X-RAY MICROANALYTICAL METHODS

3.1. Elemental composition

The major composition of individual microparticles including low atomic number (low- Z) elements can be quantitatively determined using electron probe X-ray microanalysis (EPMA) [11, 12]. However, on the basis of the major element composition natural and anthropogenic particles cannot be identified unambiguously (consider e.g., soil-derived and fly-ash particles in atmospheric aerosol). Therefore the accurate knowledge of the minor and trace composition of individual particles is of high importance for source profiling studies, as they offer more distinctive features for the identification of different particle sources. As X-rays originating from conventional diffraction X-ray tubes or synchrotron sources can be focused to form micrometre-sized beams [13], the examination of micro-particles became possible using microscopic X-ray fluorescence (μ -XRF) [14].

Either using photons or charged particles for excitation, the measured X-ray intensities of elements depend non-linearly on the concentrations, and they are not independent from each other. For this reason, no explicit mathematical expression can be given for calculating concentrations from measured intensities. The problem has to be solved in an iterative way. The conventional quantification methods [15] are not suitable for single-particle analysis, because they are not flexible enough for various experimental and sample conditions, such as the analysis of microparticles having irregular shapes and heterogeneous compositions.

It is well-known that Monte Carlo simulation is a reliable tool for modelling the matrix and geometry effects in X-ray generation using excitation either using photons or electrons for excitation of the microscopic volume of interest. Quantification can be achieved by iterative adaptation of the simulated elemental concentrations until the deviations between the simulated and experimental peak areas fall within the statistical uncertainties of the recorded fluorescent lines [12, 16].

A significant advantage of the MC simulation based quantification scheme compared to other methods, such as fundamental parameter (FP) algorithms, is that the simulated spectrum can be compared directly to the experimental data in its entirety, taking into account not only the fluorescence line intensities, but also the scattered background of the XRF spectra. This is coupled with the fact that MC simulations are not limited to first or second order approximations and to ideal geometries.

If EPMA results are available for exactly the same particle or the same particle type (including light elements such as C, N and O), the composition of the *dark matrix* considered for μ -XRF – elements in the sample not producing characteristic X-rays detectable by the μ -XRF setup – can be calculated from the major elemental composition obtained from EPMA.

Using the Monte Carlo based quantification method, the minor element content of individual microparticles can be determined using laboratory scale μ -XRF setups based on a standard diffraction X-ray tube and capillary optics. If the trace element content of the particles is demanded, micro-XRF measurements employing synchrotron radiation are necessary, using the matrix composition determined for each individual particle separately using the laboratory micro-XRF system or EPMA measurements.

The Monte Carlo based standardless quantification method for both EPMA and μ -XRF was tested using particulate standards with known composition. Relative deviations in the range of 5-20 % have been achieved by the Monte Carlo quantification scheme, depending on the analyzed element and sample type [11, 12, 16, 17].

3.2. Chemical state of selected metals

In order to estimate the environmental mobility and potential for dissolution of heavy metals, speciation analysis is necessary to determine the chemical state of these metals. For bulk samples, most of the cases sequential extraction is applied for this task [8]. An alternative method for chemical state analysis is X-ray absorption near-edge structure (XANES) spectrometry [18, 19]. In addition to its non-destructiveness, the advantage of the method is that chemical speciation information can be obtained from a microscopic volume as a single grain that can be identified as pollutant particle, even when the element of interest is present at trace concentration level [20, 21].

The XANES method uses high intensity monochromatic X-ray beams originating either from synchrotron radiation sources. From the near edge part of the absorption spectrum one can deduce information on the chemical state of the element of interest. *White line* is a sharp, line-like absorption often observed in the initial absorption rise at the edge of a semiconductor, an insulator or a semimetal. It is called a white line because its appearance on the x-ray film. Its presence masks the true position of the absorption edge. The *pre-edge peak* is also a strong, line-like absorption, but below the absorption edge. The structures above 10 eV, due to interference effects of the photoelectron wave function, determined by the elastic scattering with neighbouring atoms, can be described by multiple scattering within a small atomic cluster. The resulting *multiple scattering resonances* of the photoelectron in the continuum give rise to the XANES spectrum in the range of ~ 10 to ~ 40 eV [22]. Changes in the charge distribution around a given atom in different chemical environments can alter the binding energies of core electron orbits, so that the XANES spectrum shows a shift in the absorption edge. A more oxidative chemical environment results in deeper core state binding energies, which in turn cause an absorption edge shift towards higher energies in the XANES spectrum. The order of magnitude of the shift is around 1 - 3 eV per valence change. The presence or absence of the possible pre-edge structure and the energies of the near-edge structures (white line and multiple scattering resonance peak) are also dependent on the oxidation state of the absorbing atom.

Environmental samples – also individual microparticles – can contain the element of interest as a mixture of different chemical state forms. For this reason, the aim of the analysis is the quantitative determination of the ratio of different chemical state forms that can be achieved by different approaches. Studying exclusively the absorption edge shift is not sufficient, since the white line (1s→np transition) can overlap with the true absorption edge. If standards are measured for all the forms of the element of interest possibly present in the sample, the spectrum of the unknown can be approximated as the linear combination of the standard spectra. For separation of close lying oxidation states the least squares fitting of analytical functions to the XANES spectra provides better results than the methods mentioned above. For each oxidation state the spectrum can be approximated by the linear combination of three analytical functions: one for the white line, one for the multiple scattering peak(s) and one for the absorption edge. The approximating function was the following [20]:

$$\tau(E) = \sum_{i=1}^n \left[I_{wi} \exp\left(-\frac{(E - E_{wi})^2}{2\sigma_{wi}^2}\right) + I_{si} \exp\left(-\frac{(E - E_{si})^2}{2\sigma_{si}^2}\right) + C_i \left(\frac{1}{\pi} \arctan \frac{E - E_{ei}}{\Gamma_i / 2} + \frac{1}{2} \right) \right] \quad (1)$$

where n is the number of the oxidation state forms, I_{wi} and I_{si} are the heights of the white line and the resonance scattering peaks for the i^{th} oxidation state, σ_{wi} and σ_{si} are the corresponding widths, E_{wi} and E_{si} are their maximum energy, C_i is the height of the absorption edge, E_{ei} is the energy of the inflexion point and Γ_i is the parameter of the arctangent step. For the single particle spectra where the self-absorption was negligible, the best fitting results were obtained when the shape of the white line was approximated as a mixture of Lorentzian and Gaussian contributions [20]. As an example, least-squares fitting of analytical functions is demonstrated on an As K-edge micro-XANES spectrum of an uranium mine tailings particle, considering As in pyrite, As(III) and As(V) forms (Fig. 1).

3.3. Identification of crystalline phases

As a complementary method, microscopic X-ray diffraction (μ -XRD) can be applied for identification of the crystalline phases in a microscopic volume such as an individual environmental particle. In contrary to XANES that probes local structure around atoms of a specific element of interest, XRD probes long-range order in the whole sample. The wavelength of X-rays is in the order of magnitude of spacing of the layers of atoms in crystalline materials, therefore the X-ray beam is diffracted on crystalline materials as three-dimensional lattices.

The basic relationship of XRD is given by the Bragg equation:

$$n\lambda = 2d \sin\theta \quad (2)$$

where λ is the wavelength of the radiation, d is the distance between lattice planes, and 2θ is

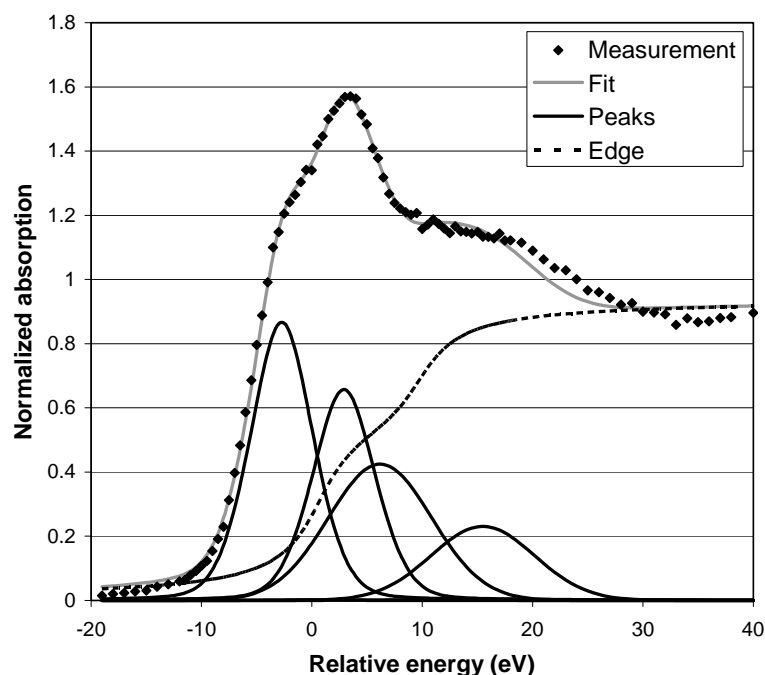


Figure 1. Fitting of the arsenic-K μ -XANES spectrum of an uranium mine tailings particle using analytical functions for the near-edge structures.

the diffraction angle. The powder diffractogram recorded from polycrystalline samples is characteristic for its crystalline phases; the positions of the peaks are suitable for identification of the phases, based on library diffraction patterns. The peak intensities are proportional to the amount of the crystalline phases. Using XRD, amorphous phases can only be identified indirectly. Complementary information on the elemental composition of the particle/grain obtained by EPMA or, micro-XRF methods help in the identification of crystalline phases.

4. EXPERIMENTAL

4.1. Samples and sample preparation

Surface sediment and water samples were collected through a 4-years survey (2000 - 2003) from rivers of the Hungarian section of the Tisza catchment area – Tisza, Szamos and Túr. Tailings samples were collected between 2005 - 2006 years from the uncovered part of the tailings pond no. I of the uranium mine under recultivation. This tailings pond was completely covered with clay and loess at the end of 2008. The selection of “hot samples” for further single-particle analysis was based on bulk chemical analyses. The pre-selected sediment and tailings samples were dried at room temperature and the particles were suspended in *n*-hexane containing rubber cement. In order to break large particle agglomerations into individual particles, the suspension was subjected to ultrasonic vibration. The suspensions as well as the

water samples were filtered through 47 mm diameter 0.4 μm pore size Nuclepore polycarbonate membrane filters. These filters were found to be suitable for X-ray microanalytical methods as well as visualization of the particles using an optical microscope.

4.2. Measurement setups for microbeam X-ray methods

The experiments were performed at the μ -fluorescence beamline L of HASYLAB (Hamburg, Germany) [23], using both white beam and monochromatic excitation. At the first case, a 70 μm diameter white beam from a bending magnet was used for μ -XRF measurements. The low-energy X-ray photons of the exciting radiation were suppressed using a 4 mm thick Al absorber. The beam size was determined using tungsten cross-slits. The fluorescence yield was detected at an angle of 90° to the incoming beam using an energy-dispersive HPGe detector. X-ray spectra were collected from selected individual particles; the trace composition was determined using the fundamental parameter method [24], and refined by Monte Carlo simulations. This experimental setup allowed the quantification of trace lanthanide elements using their K lines.

At the second case, the white beam was monochromatized to 19 keV using a NiC multilayer monochromator, with an energy resolution of 10^{-2} . An X-ray microbeam of 15 μm diameter was formed using a single-bounce glass capillary for the μ -XRF measurements. The X-ray micro-beam was focused to the focal plain of the optical microscope used for on-line visualization of the sample. The fluorescence yield was detected using an energy-dispersive silicon drift detector (Radiant Vortex SDD).

Two-dimensional X-ray intensity maps were recorded for each pre-selected particles, using a 5 s acquisition time for each pixel. X-ray spectra of each pixel were evaluated by non-linear least-square fitting using the AXIL software package [25], and two-dimensional elemental maps were constructed from the resulting net X-ray intensities. The coordinates of the maximum positions of the element of interest was recorded for further X-ray absorption measurements using a modified set-up. The μ -XRD images were recorded using a MarCCD camera. Corundum and silicon samples were measured for calibration.

The μ -XANES measurements were carried out using a modified setup employing a monochromator with higher energy resolution and capillary optics providing higher X-ray intensity at the focal spot. The white beam was monochromatized by a Si(111) double monochromator with an energy resolution of around 10^{-4} . A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of 1 mm^2 down to a spot size of 15 μm diameter. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the K absorption edge of Mn, Zn and As (6539, 9659 and 11867 eV) and the L_3 absorption edge of U (17167 eV) by stepping the Si(111) monochromator, while the $K\alpha$ and $L\alpha$ fluorescent yield of the element of interest was detected. The used energy step size varied

between 0.5 (edge region) to 2 eV (more than 50 eV above edge). Minerals and compounds generally present in soil, sediment, uranium and gold mine tailings were selected as standards, prepared from minerals and *pro analysis* grade chemicals. The U-L₃ and Zn-K μ -XANES spectra were evaluated using linear combination of standard spectra, while the As-K μ -XANES spectra were evaluated using analytical functions [20].

EPMA measurements of individual particles on filters were carried out on a Jeol 733 electron probe microanalyzer equipped with an Oxford ultrathin-window EDS detector, which allows the measurement of C and O as well. The resolution of the detector is 133 eV for Mn-K α X-rays. The localisation and selection of individual particles for X-ray analysis were based on the backscattered electron (BSE) signal, because of its strong atomic number dependence: particles usually have BSE signals above a pre-selected threshold level. An accelerating voltage of 10 kV and a beam current of 1 nA was chosen for all the measurements. In order to obtain a statistically significant number of counts in the X-ray spectra, a typical measuring time of 20 s was used. Morphological parameters such as diameter and shape factor were calculated by the image processing routine of the measuring program. The characteristic X-ray spectra obtained from the particles have been evaluated using the AXIL code [25]. The calculation of the particle composition including light elements was performed by a reverse Monte Carlo method [12].

5. APPLICATION EXAMPLES

The use of non-destructive microanalytical techniques based on scanning electron microscope and synchrotron radiation makes a complex characterisation of individual particles possible. As application examples of the combination of methods, characterisation of pollution related particles in the water and sediment of River Túr, as well as uranium-rich particles in the abandoned uranium mine tailings are discussed. After selection of the most appropriate samples using bulk analytical methods, individual particles having high heavy metal content had to be identified. In case of river Túr, the particles characteristic to the heavy metal pollution had also specific morphology. They could be easily identified on optical or electron microscopic images [26]. For the identification of U-rich particles on the Nuclepore filter, laboratory micro-XRF measurements as well as the use of solid state nuclear track detectors provided efficient ways [27]. After identification, the particles could be easily relocated for further non-destructive μ -XRF, μ -XANES and μ -XRD investigations at synchrotron radiation beamlines.

5.1. Polluting particles in river Túr

River Túr is a small tributary of river Tisza, originating in north-western Romania. Although the Tisza river was affected by water pollution due to two major mining accidents occurred in

the Romanian part of the catchment area at the beginning of 2000, the concentration of heavy metals in sediments and suspended particulate matter (SPM) decreased to the mineral background level one year after the pollution event [28]. In the tributaries Szamos and Túr, however, no significant decrease of the heavy metal concentrations was observed in the recent years. Permanent pollution of inorganic microcontaminants (like heavy metals) originates from mining, industrial, agricultural activities and municipal sewage discharges. A major part of permanent pollution originates from the upstream countries of the catchment area. The high zinc level in River Túr was in particular also noticed by the local water authority.

In the SPM samples collected from river Túr, strange fibres were observed by electron microscope (Fig. 2), these particles were aluminosilicates containing around 19 wt% Mn and 15 wt% Zn (Fig. 3). This particle type was observed in samples collected in 2001, 2002 and 2003. Some particles were found in the surface sediment as fragments of these fibres.

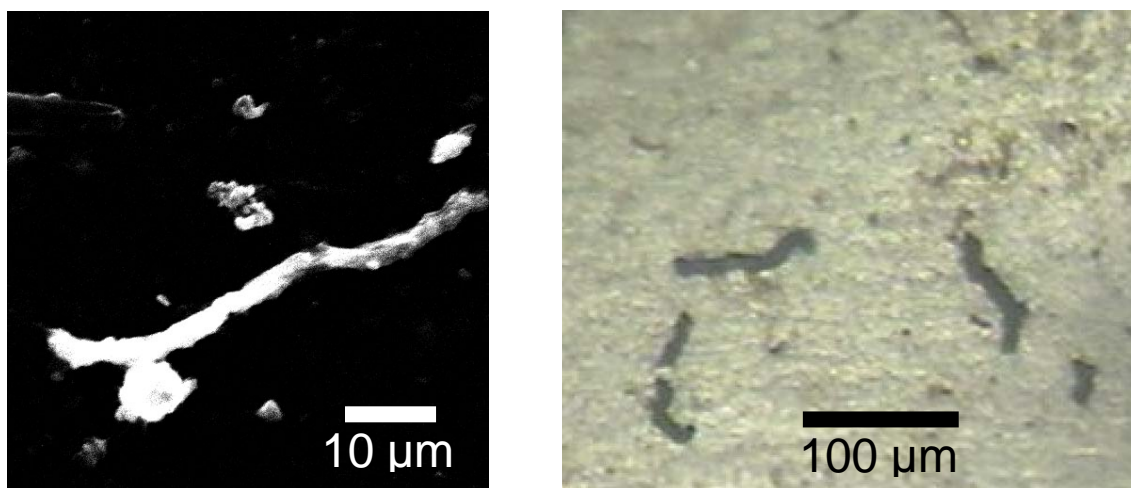


Figure 2. Secondary electron image (left) and optical image (right) of typical fibres identified in SPM of river Túr.

As the Zn pollution could be related to one characteristic particle type, the more sensitive synchrotron-based single-particle methods could be applied in a very effective way. As a highly toxic and bioavailable element, Cd was found to be connected to the fibres (Fig. 4).

Zn and Mn K-edge XANES spectra collected from bulk sediment and reference compound samples are shown in Figs. 5 and 6, respectively, compared to μ -XANES spectra of the fibre-shaped pollution particles. In the case of zinc (Fig. 5) there is no striking difference between the chemical environment of Zn in bulk sediment and the single particles characteristic for the pollution. Linear combination of standard spectra showed that 55 % of Zn was connected to carbonates and 45 % to silicates. Among silicates, in the bulk sample

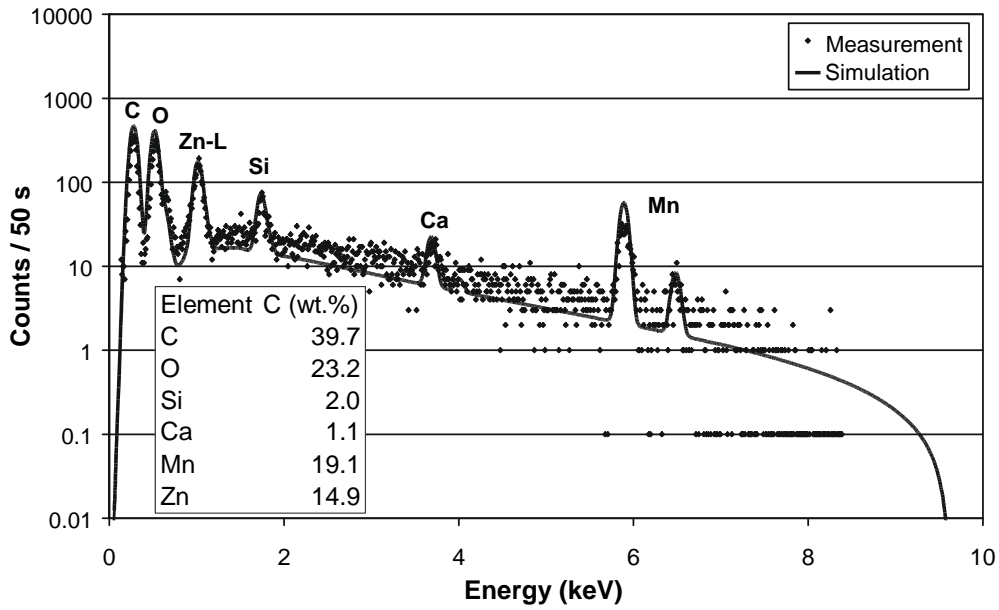


Figure 3. Measured and simulated EPMA spectra and major elemental composition calculated by the MC method, for a typical fibre particle from the SPM of Túr.

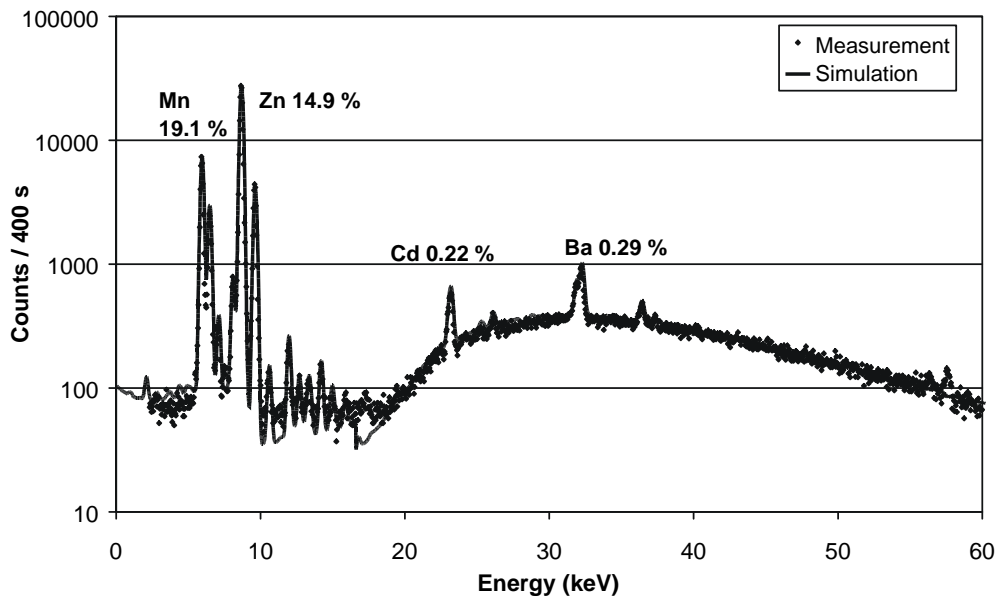


Figure 4. Measured and simulated white beam μ -XRF spectra for a typical fibre particle from the SPM of river Túr.

only Zn containing phyllosilicates were detected, but the fibre particles contained 20 % of zinc as willemite.

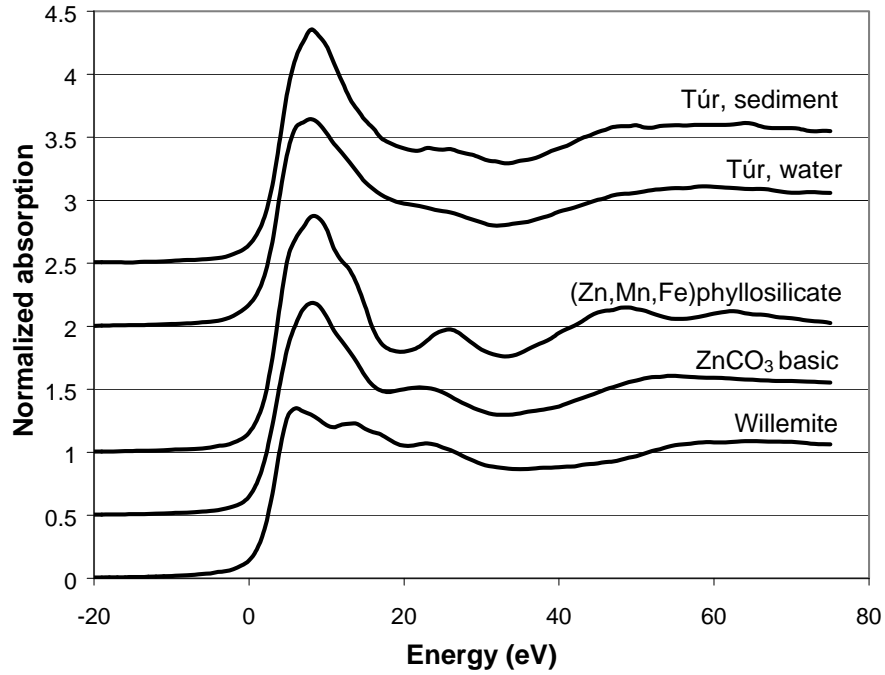


Figure 5. Zn K-edge (μ -)XANES spectra of bulk sediment, individual fibre particles from the SPM of river Túr, compared to standard spectra.

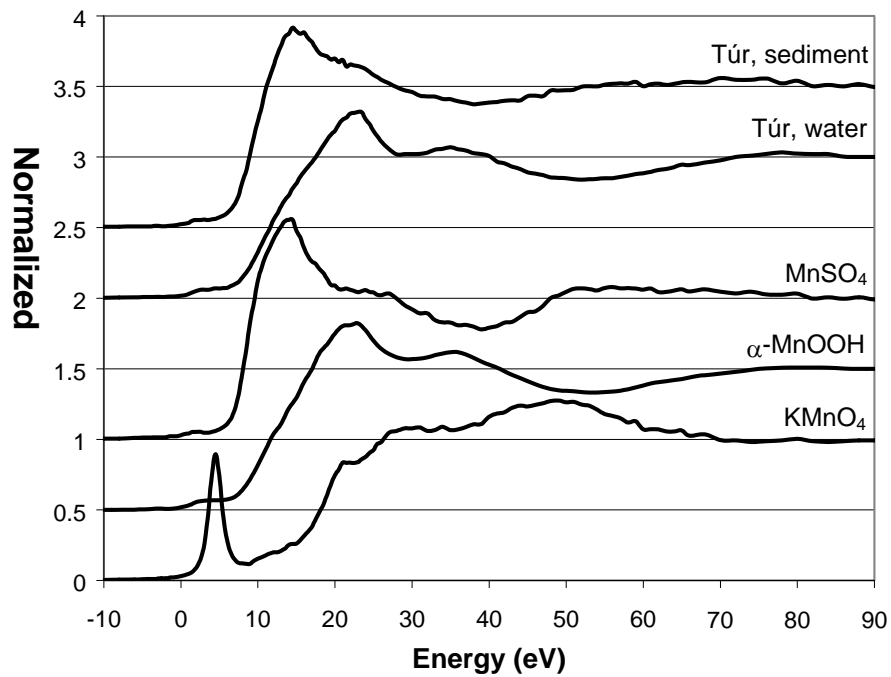


Figure 6. Mn K-edge (μ -)XANES spectra of bulk sediment, individual fibre particles from the SPM of river Túr, compared to standard spectra.

Mn was found in Mn (III) oxyhydroxide form in the fibre particles, while in the bulk sediment collected from the same place only Mn (II) compounds were present. The presence of Mn (III) oxyhydroxide was verified with micro-XRD measurements, indicating that Mn is present in an amorphous phase. Mn (III) oxyhydroxide can remove heavy metals from the water solution by complexation processes. The latter result indicates that a major part of the heavy metal pollution arrives to the Túr River in the water phase; this was supported by measurements of the dissolved Zn content of the Túr water, being above 70 $\mu\text{g/l}$ [26]. Immediately the river entering Hungary at Kishódos, a high Zn concentration was observed in the surface sediment indicating that the continuous Zn pollution arrives from Romania. The intense mining activities at the Turt mine being the most probable cause of the continuous pollution [26].

5.2. Uranium mine tailings particles

The re-location of the preliminary located uranium-rich particles was easier and faster in the view-field of the optical microscope at the measurement setup of the synchrotron beamline. After the re-location, elemental maps were collected over the individual uranium-rich particles, because not only the average uranium concentration changed in a large range comparing different particles, but even the internal heterogeneity within one particle. As an example, X-ray intensity maps of a selected U-rich particle generated from the characteristic X-ray lines of sixteen elements as well as from elastic (Rayleigh) and inelastic (Compton) scatter peaks can be seen in Fig. 7.

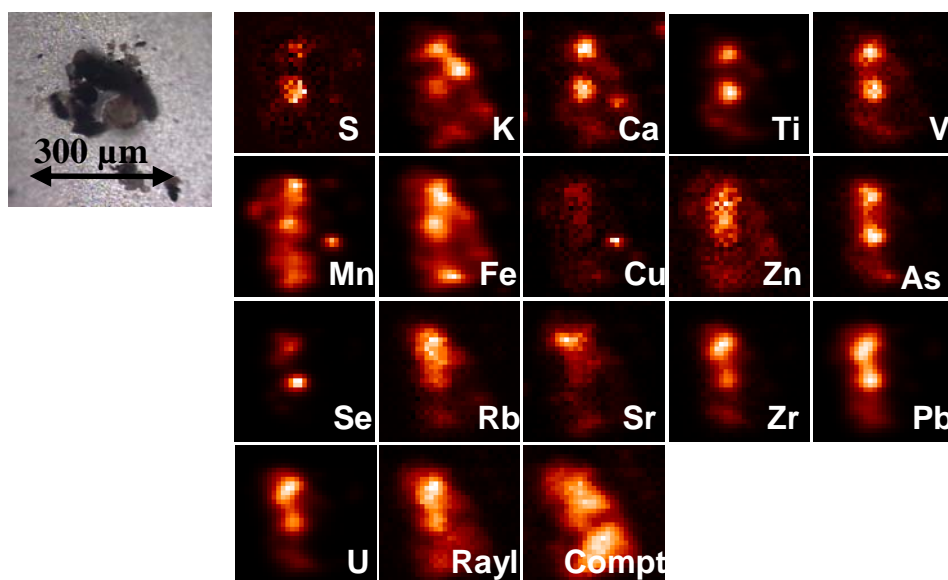


Figure 7. X-ray intensity maps collected from a 300 μm U-rich particle (optical image on the left) using a step size of 10 μm .

The whole particle is visible in the scatter maps indicating that there is no significant difference in the density and in the average atomic number over the particle. The elemental maps, shows large heterogeneity, and showing “hot spots” with much higher intensity of that element compared to the rest of the particle. Uranium shows distinct maximums, indicating that it is enriched in a relatively smaller part of the particle. The distribution of titanium, vanadium, arsenic, selenium, zirconium and lead is similar to that of uranium. Correlation was found between the distribution of U and an other toxic metal As in almost all the individual particles, however the ratios of the X-ray intensities are different in different regions. All the uranium-rich particles separated from the tailings sludge showed similar results. They showed heterogeneous uranium and arsenic distributions in the particles and showed correlation between the As-rich and U-rich parts of the particles. A μ -XRF spectrum collected at the position of U maximum of the particle in Fig. 7 is shown in Fig. 8.

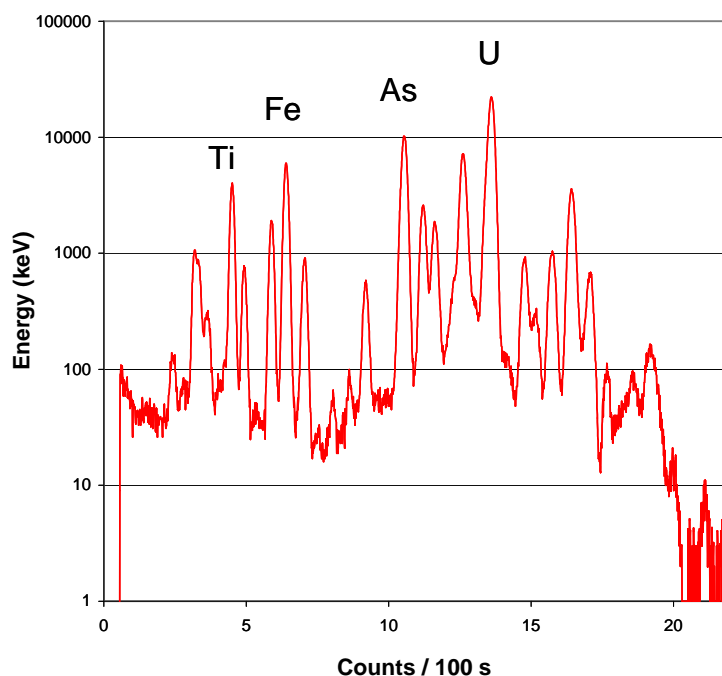


Figure 8. μ -XRF spectrum collected at the maximum position of the U distribution.

Environmental mobility of heavy metals strongly depends on their chemical state. In order to study the oxidation state of uranium and arsenic, μ -XANES spectra were collected at the maximum positions of the uranium distribution in the pre-selected individual particles. The resulted U-L₃ edge and As-K-edge μ -XANES spectra collected from three individual particles and standards are shown in Figs. 9 and 10, respectively.

As a whole, 50 - 80 % of uranium was found in the reduced, less mobile U (IV) form in the mine tailings particles studied [29]. High amount of As (30 - 60 %) was found in the less

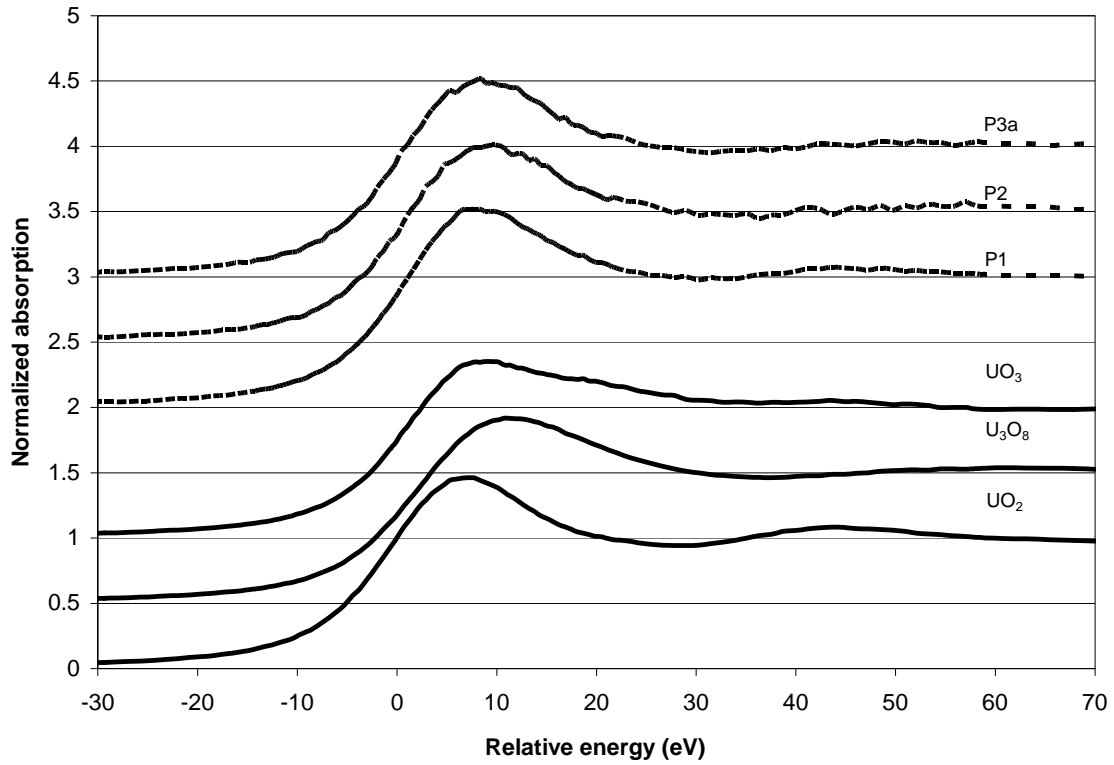


Figure 9. U-L₃ edge μ -XANES spectra of three selected individual tailings particles and standards.

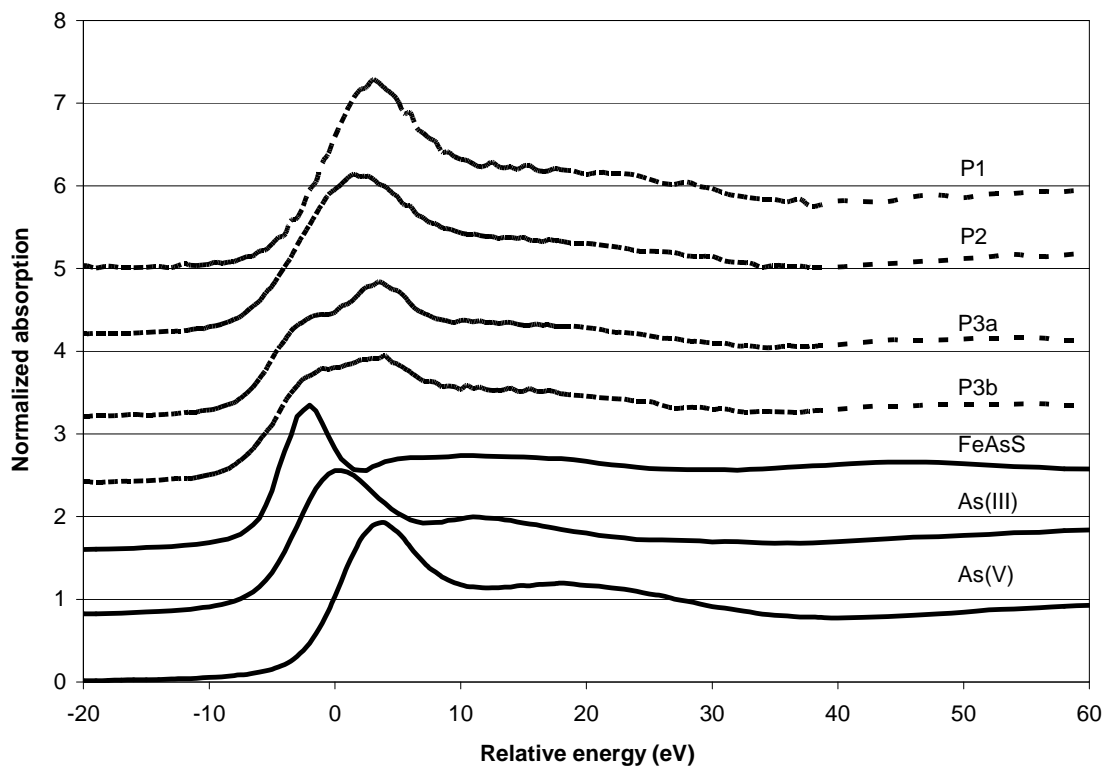


Figure 10. μ -XANES spectra at the arsenic K-edge collected from different particles and standards.

mobile As (V) form in all tailings particles, but some of them contained arsenic also as As in pyrite [30]. For the latter particles, μ -XANES and μ -XRF results are in accordance, since high correlation was found between the Fe and As distributions. A few particles contained high amount of As (III), which is 60 times more toxic and generally more mobile than As (V). Table 1 shows the oxidation state of arsenic and uranium in particles P1, P2, and P3. By comparison of the oxidation state of As and U in the same analyzed particles, finally two groups of tailings particles were found. The highest amount of the U (IV) form was detected in particles where As was present mostly as connected to pyrite, while the second group of particles contained As (III) and higher amount of U_3O_8 .

Table 1. Demonstration of ratios of uranium and arsenic species in exactly the same three individual particles based on As-K and U-L3 μ -XANES spectra.

Particles	P1	P2	P3a	P3b
UO₂ (%)	60	47	69	69
U₃O₈ (%)	40	53	31	31
UO₃ (%)	-	-	-	-
As in pyrite (%)	-	-	57	58
As (III)(%)	67	44	-	6
As (V)(%)	33	56	43	36

The mineral phases identified by μ -XRD in the same particles were consistent with the oxidation states of As and U determined by μ -XANES. For example, 69 % of uranium was present as U (IV) and 58 % of arsenic was present as As in pyrite in particle P3. These results were verified with μ -XRD analysis, since uraninite and pyrite minerals were identified, amounting 5 and 40 %, respectively, of the crystalline phases in the particle (Fig. 11).

μ -XRF, μ -XANES and μ -XRD are efficient methods for characterising the heterogeneity of the particles, correlation between the chemical state of uranium and arsenic in the same individual particles. However, they need careful selection of sample areas or particles to be analyzed. Information on the mobility and solubility of As and U is important, because they are toxic elements and the location of the tailings ponds is between two water basins. In mobile form they can risk the water basin and the public health.

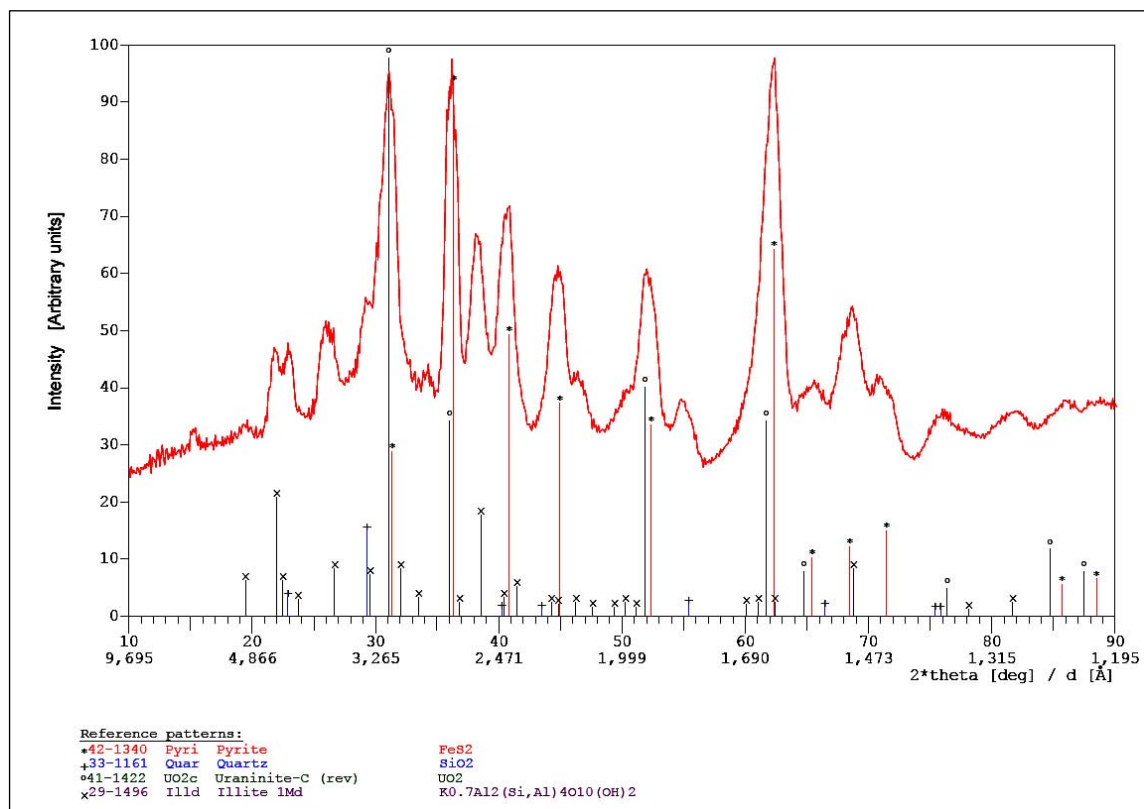


Figure 11. Integrated diffraction pattern indicating the peaks of the identified minerals.

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