

Evaluation of major and trace elements present in extracted humic acid from bog peat

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Abstract. The human consumption of humic acid is increasingly relevant therefore the knowledge of exact composition is essential. To make a step in that direction we present gap filling results obtained from three different element analytical investigations of humic acid extracted from fen peat examined in the Carpathian Basin. Prompt-gamma activation (PGAA), neutron activation analytical method (NAA) and X-ray fluorescence (XRF) analysis was carried out. After presenting and explaining the essence of used analytical methods we show some collected spectra and a table where all the concentration of the identified elements are presented with the corresponding measurement errors. All together 42 elements were identified.

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1 Introduction

In our modern life, due to fertilizers, additives or soil pollutions less and less nutritious, vegetables, fruits and grains contain sufficient natural vitamins and trace elements which would be essential for a balanced human diet. In particular, proper intake of trace elements are problematic. As solution a natural source could be the humic acid, which is known from a long time. There are numerous monographs available [1–3] which deal with the basic structure and properties of various humic substances. The aim of our recent research is the determination of the major and minor trace elements in humic acids by means of various analytical methods. The researcher Mr. Pádi applies this kind of humic acid in dietary supplements, storages and solid conditioners sometimes with various additional vitamins and herbs. During such production processes the knowledge of precise elements composition is essential. There are some infrared spectroscopic investigation of elemental composition of humic acids available from different groups [4–13]. However these studies concentrate only on the elemental compositions of H,C,N,S and O. To our knowledge there is no analytical data avail-

able where the precise concentration of additional trace elements are determined. In addition to determining the humic acid composition there are numerous studies available which investigates other properties of humic acids like the determination of absorption isotherms [14], the interaction with contaminants [15] the thermal properties [16] or acylation [17]. In this research we present the major and trace element concentrations in humic acid. We compare the results of three independent element analytical measurements of prompt-gamma activation (PGAA), neutron activation analysis (NAA) and X-ray fluorescence (XRF).

Our investigated humic acid originates from the Carpathian Basin. The raw material (which is now the bog peat) was surface minded from close to the village of Nagyvázsöny in the region of Transdaubia. Bog peat is located directly below the surface of the soil and is therefore free from any further contamination such as atmospheric fall-out. Peat or with other name turf is an accumulation of partially decayed vegetation or organic matter.

The investigated humic acid probes were manufactured by Mr. Gy. Pádi from bog peat according to the National Patent of [18]. The investigated material itself is a grayish brown not burning powder with very low solubility even in strong acids and alkalis.

The chemical composition of humic acid is a complicated question, is the subject of numerous research studies [19,20] and can be defined as a separate science.

2 Materials and methods

Humic acid samples were analyzed with neutron activation analytical methods (NAA), prompt-gamma activation (PGAA) method and X-ray fluorescence (XRF) analysis. Among others these are instrumental multi-element analysis procedures [21] which are in some cases capable to detect atomic concentrations which are much below the usually applied chemical methods.

The first two measurements were performed at the Budapest Neutron Centre (BNC) [22]. The PGAA and NAA facilities are operated by the Nuclear Analysis and Radiography Department, Centre for Energy Research, Hungarian Academy of Sciences. The methods were validated by numerous geological reference standards, and by inter-laboratory comparison. At the Budapest Neutron Centre both NAA and PGAA are using the k_0 -standardization method, which does not require a standard for analysis. As third, X-ray fluorescence (XRF) method was also applied. The measurements were performed in the Environmental Physics Laboratory at the Centre for Energy Research, Hungarian Academy of Sciences.

2.1 NAA

Neutron activation analysis (NAA) is a method for quantitative composition analysis of chemical elements, based on the partial conversion of stable nuclei in the sample to radioactive nuclei by known nuclear reactions. This is followed by the quantization of the reaction products via their gamma radiations. The selective measurement of the radiation gives quantitative and qualitative information about the produced radioactive atoms. The NAA is especially capable of trace element determination in $\mu\text{g/g}$ concentration range or below. NAA method requires only simple sample preparation. For the measurement only small amount of sample needed, however the irradiated samples become radioactive, that it cannot be returned to the owner. For k_0 -NAA irradiation, 108 μg humic acid powder sample were heat-sealed in high-purity quartz ampule (Suprasil AN, Heraeus). The quartz ampule was wrapped in aluminum foil and in a set with 5 other powder samples were encapsulated in an aluminum container, irradiated in a rotating, well-thermalized channel of the Budapest Research Reactor (BNC) for 3 hours. With the samples, monitor foils of Au, Zr were co-irradiated to get the flux parameters, which are essential to the concentration calculations by the k_0 -method. The thermal neutron flux density of rotating irradiation channel (N17) has been $1.86 \times 10^{13} \text{cm}^2 \text{s}^{-1}$. Prior to the gamma counting, the irradiated quartz vials were surface cleaned by chemical etching in 10 % hydrogen fluoride acid solution, washed with double distilled water and finally dried. The gamma

radiation of the humic acid sample was counted twice. After a typical decay time of 4 days, the gamma spectrum was collected for 900 sec, at 10 cm from the detector top. To improve the detection limit for several radionuclides, a second measurement was made after 20 days, when the spectrum was measured for 6600 sec, at 5 cm from detector top. The gamma-rays emitted from the samples were counted within low-level counting chambers (to reduce the room background), with a carefully calibrated p-type Ortec PopTop HPGe detector, having an energy resolution of 1.75 keV and relative efficiency of 55 % at 1332 keV, operated in a 50-3300 keV energy range. The detector was connected to a dual-input ORTEC DSPEC 502 spectrometer, and read out by the ORTEC Maestro 7 software. The spectra with $2 \times 16 \text{ k}$ channel were recorded with the zero-dead time (ZDT) option to accurately account for the different time dynamics of the isotopes [23]. The corrected and uncorrected halves of the spectra are stored in a single SPC file. For spectrum evaluation HyperLab 2013.1 software was used [24]. For identification of radioactive isotopes and for element concentration calculations KayZero for Windows 3.06 program [25] was applied, which is able to determine thermal and epithermal neutron flux ratio (f), alpha, and F_c calculation factors. KayZero calculates concentrations using the k_0 -standardization method according to [26].

2.2 PGAA

Prompt gamma activation analysis is also a nuclear analytical technique for non-destructive determination of elemental and isotopic compositions [27]. The sample is irradiated in a guided neutron beam, and the gamma-rays from the radiative capture are detected. All elements can be analyzed (except for helium), without any prior information on the analyte. The energies and intensities of the peaks are independent of the chemical state of the material; hence the analytical result is free of any matrix effects. Both neutrons and gamma-rays are highly penetrating; therefore, the average composition of the entire illuminated volume is obtained. For PGAA analysis, 6 g-portion was weighted and heat-sealed into Teflon bags. The neutron flux at the sample position of the PGAA station was about $9.6 \times 10^7 \text{cm}^2 \text{s}^{-1}$. The cross-section of the neutron beam was adjusted to 2020 mm^2 to optimize the count rate. The gamma radiation from the radiative neutron capture was detected with a High-Purity Germanium (HPGe) detector, surrounded by a Bismuth Germanate (BGO) scintillator and 10 cm thick lead shielding for 10 hours; the signals were processed with a Canberra AIM 556A multichannel analyser. The facility have been described in details in an earlier publication [28]. The spectra was evaluated with Hypermet-PC gamma spectroscopy software. The element identification was done with the ProSpeRo program, utilizing our prompt-gamma analysis library [29].

2.3 XRF

X-ray fluorescence (XRF) analysis was carried out on pressed pellets of humic acids using an in-house system comprising of X-ray tube and secondary target in Cartesian geometry. 20 mm diameter pellets were pressed containing 0.5 to 1 g of humic acid material. The tube-excited XRF measurements were performed using a Seifert diffraction tube with Mo anode and Mo secondary target. The X-ray spectra were collected by a KETEK (Munich, Germany) silicon drift detector with an energy resolution of 150 eV for Mn-K X-rays. The typical measuring time was 15000 s. The characteristic X-ray spectra obtained from the samples were evaluated by non-linear least-squares fitting, using the AXIL code [30]. For quantitative analysis, the sensitivity curve of the measurement system was determined by measuring a series of Micromatter (Surrey, BC, Canada) standard thin foils. The precision and accuracy of the method for pressed pellets was tested by certified reference materials [31,32].

The appropriate quantification of heavier minor and trace elements requires knowledge on the major, light element composition of the samples, called as dark matrix in XRF since X-ray lines of light elements do not appear in the X-ray spectrum. Matrix absorption corrections were therefore made based on the major composition of humic acids determined by complementary methods [33].

3 Results and discussion

In this section we present and compare the quantitative results obtained by recording the different spectra with the NAA, PGAA and XRF methods, respectively. We summarize the obtained experimental data in table 1 so that the results of the three different measurement methods can be easily compared. We present the measured concentrations with the systematic errors, and the three ratios. The elemental concentrations are given in $\mu\text{g/g}$ SI units, with absolute ($\mu\text{g/g}$) and relative (%) uncertainty. PGAA could detect 20 different elements from H up to Gd. The largest measured concentrations have O, Si, H, Ca and C. The largest measured uncertainties have the elements of Br, Nd, V, Mg and Cd. This is reasonable for a geological organic sample.

The NAA method detected altogether, concentration of 24 elements (Ca, K, Fe as major components; Ba, Sr, Nd, Na as minor components; some rare-earth elements: La, Ce, Sm, Eu; actinides: Th and U; transition metals: Co, Cr, Hf, Sc, Ta, Zn; alkali metals: Cs, Rb; nonmetals: As, Sb; and Br as halogens) could be quantified by NAA method, with a relative uncertainty below 10%. Elements with the largest relative uncertainty are Ba, Sr and Ca above 7%. The detected elements with the largest absolute concentrations are Ca and Fe which is again a reasonable result for a geological organic sample. The schematic spectra collected with the NAA method is presented in Fig. 1. It is clear that this method identifies the largest number of trace elements. NAA and PGAA are complementary nuclear analytical techniques, and as few elements detectable

by both methods, the results are comparable. Most elements analyzed by PGAA releasing prompt-gamma rays after neutron capture, and resulting short lived isotopes. The NAA measuring protocol, requires longer decay time, thus the short lived isotopes are impossible to detect. However, elements sensitively analyzed with NAA, requires activation with high neutron flux, and producing longer lived isotopes releasing gamma rays detected days after irradiation. Table 1 contains the concentrations of the major elements (in oxide and elemental form in wt%), and the trace elements (in $\mu\text{g/g}$) together with their relative 2σ ($k = 2$) uncertainties. The measurement is non-destructive, and the induced radioactivity is low and decays in few hours or in 1-2 days, so samples can be given back to owners.

The final, third method was XRF. With this technique concentrations of 17 minor and trace elements could be determined. The largest measured absolute concentrations are Ca, S and Fe. The presence of Br at elevated concentration in the humic acid samples is clearly visible in the X-ray spectra (Fig. 2.), where a spectrum of 0.5 g clean boric acid is plotted for comparison. It should be noted that boric acid pellet was used as a blank, correction especially for Pb and Cu was important. This method was able to detect the least number of elements.

Finally we analyze the available concentration ratios of the introduced methods. Only for the four elements of K, Ca, Fe and Br could be detectable by all three methods. It is also clear from the last two columns of Table 1 that the measured concentrations of XRF are in most cases lower than the two other methods. The only exception is Br. From the 9th column of Table 1 it looks clear that measured NAA concentrations are in most cases are lower than the measured PGAA concentrations. The three exceptions are Br, Nd and Sm. The last two elements are heavy, hard to identify with NAA and PGAA and have a tinny measured concentration compared to lighter elements. It is interesting to see that even Pb and U are present in humic acid and can be detected with XRF.

Z	El	PGAA		NAA		XRF		$\frac{c(NAA)}{c(PGAA)}$	$\frac{c(XRF)}{c(PGAA)}$	$\frac{c(XRF)}{c(NAA)}$
		$c [\mu g/g]$	$\delta c [\%]$	$c [\mu g/g]$	$\delta c [\%]$	$c [\mu g/g]$	$\delta c [\%]$			
1	H	38200,00 ± 1973,18	5,17							
5	B	77,60 ± 4,03	5,19							
6	C	354400,00 ± 19059,25	5,38							
8	O	478300,00 ± 23902,58	5,00							
11	Na			979,00 ± 17,88	1,83					
12	Mg	4790,00 ± 388,53	8,11							
13	Al	9570,00 ± 566,96	5,92							
14	Si	39100,00 ± 2232,43	5,71							
16	S	29600,00 ± 1640,43	5,54			5240,00 ± 700,00	13,36		0,18	
17	Cl	221,00 ± 12,15	5,50							
19	K	2610,00 ± 145,60	5,58	2440,00 ± 80,45	3,30	1340,00 ± 160,00	11,94	0,93	0,51	0,55
20	Ca	36400,00 ± 2194,13	6,03	35170,00 ± 2618,00	7,44	33800,00 ± 630,00	1,86	0,97	0,93	0,96
21	Sc			1,71 ± 0,03	1,75					
22	Ti	591,00 ± 34,89	5,90			377,00 ± 29,00	7,69		0,64	
23	V	47,60 ± 4,87	10,23							
24	Cr			12,42 ± 0,40	3,22					
25	Mn	156,00 ± 9,49	6,08			79,00 ± 15,00	18,99		0,51	
26	Fe	5880,00 ± 335,12	5,70	5739,00 ± 111,00	1,93	3760,00 ± 32,00	0,85	0,98	0,64	0,66
27	Co			2,12 ± 0,06	2,83					
28	Ni					3,00 ± 0,40	13,33			
29	Cu					0,70 ± 0,30	42,86			
30	Zn			20,90 ± 1,05	5,02	9,70 ± 2,50	25,77			0,46
31	Ga					0,50 ± 0,10	20,00			
33	As			5,77 ± 0,18	3,12	3,10 ± 0,40	12,90			0,54
35	Br	2,43 ± 0,66	27,16	86,12 ± 1,56	1,81	51,80 ± 4,40	8,49	35,44	21,32	0,60
37	Rb			15,20 ± 0,80	5,26	9,80 ± 0,70	7,14			0,64
38	Sr			189,40 ± 14,72	7,77	131,00 ± 10,00	7,63			0,69
39	Y					1,70 ± 0,40	23,53			
48	Cd	0,16 ± 0,01	6,13							
51	Sb			0,45 ± 0,03	6,67					
55	Cs			2,38 ± 0,05	2,10					
56	Ba			183,10 ± 14,21	7,76					
57	La			4,60 ± 0,10	2,17					
58	Ce			11,62 ± 0,32	2,75					
60	Nd	1,51 ± 0,33	21,85	421,00 ± 13,43	3,19			278,81		
62	Sm	0,75 ± 0,04	5,33	0,79 ± 0,02	2,53			1,05		
63	Eu			0,17 ± 0,01	5,88					
64	Gd	0,85 ± 0,06	7,10							
72	Hf			0,67 ± 0,03	4,48					
73	Ta			0,16 ± 0,01	6,25					
82	Pb					2,80 ± 0,30	10,71			
90	Th			1,56 ± 0,05	3,21					
92	U			7,12 ± 0,20	2,81	5,70 ± 0,60	10,53			0,80

Table 1. The comparative summary of the three measurements

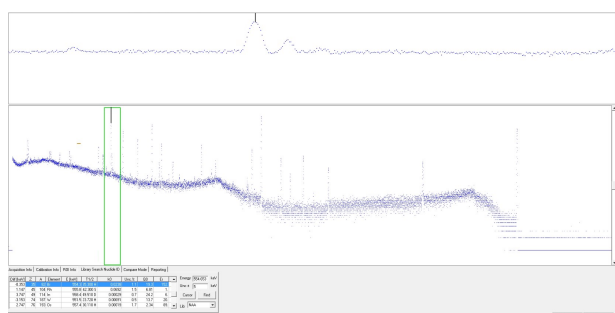


Fig. 1. The Gamma spectra of the NAA method collected for the humic acid as it is presented in the Hyperlab software.

4 Summary and conclusions

After the introduction of humic acid as a compound natural material we gave a technical description of three different element analytical methods the NAA, PGAA and XRF. All these methods were applied to study the major

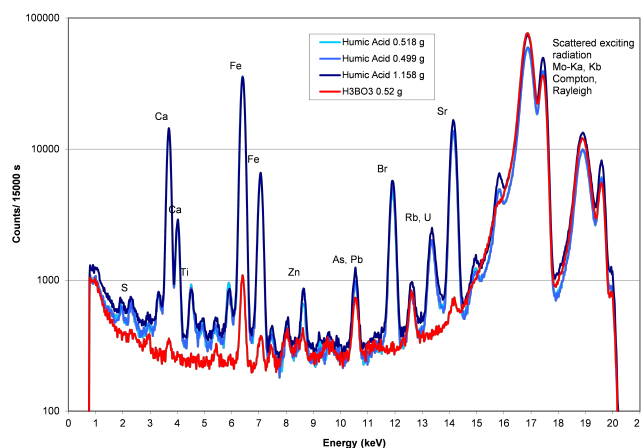


Fig. 2. X-ray spectra collected from humic acid pellets of 0.5-1.1 g compared to a blank X-ray spectrum of 0.5 g boric acid.

and trace element spectra of our humic acid sample. Beyond the most relevant organic elements (H,C and O) the major components of the investigated humic acid are Ca, Si, Fe and S. Concentration of biologically relevant trace elements eg. Na, Mg, V, Cr etc. were measured which is an essential knowledge for food supplements and storage of soil conditioners. All together 42 different elements were detected. NAA could detect 24 different elements, PGA 20 elements and XRF 17 elements. It is interesting that even the presence of U and Th can be detected. All three methods found a relatively high concentration for Fe and Ca which is a good news because these are essential for humans. Luckily, we detected Zn and Cr which are important and desirable trace elements for humans. Humic acids contain metal atoms in chelate bondings which allows the human body to absorb and bind them. Further work is in progress, we plan to analyze our humic acid samples with additional Raman, Mössbauer and atom absorption spectroscopy.

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