Original Research Article

# Major and trace elements in the humic acid

**Abstract.** We present precise analysis of major and trace elements of the humic acid. We used three different element analytical techniques in our investigations as prompt-gamma activation analysis (PGAA), neutron activation analysis (NAA) and X-ray fluorescence (XRF) analysis was carried out. We identified 42 elements in our sample.

**PACS.** 78.70.En, 78.70.Nx,78.90.+t X-ray emission spectra and fluorescence, Neutron inelastic scattering, Other topics in optical properties, condensed matter aspect

## 1 Introduction

During the last decades large interest is turned to the use of humic acids. There are numerous monographs available [1–3] which deal with the basic structure and properties of various humic substances. The aim of our present research is the determination of the major and trace elements in humic acids by means of various analytical methods. One of us Mr. Gy. Pádi applies the humic acid in food supplement, storage and solid conditioners sometimes ~~together~~ with various vitamins and herbs. Therefore the pre- cise elements composition is essential. There are some in- frared spectroscopic investigation of elemental composi- tion of humic acids available from different groups [4–13]. However these studies concentrate only on the elemen- tal compositions of H, C, N, S and O. To our knowledge there are no analysis available where the concentration of additional trace elements ~~are determined as well~~. In this work we present the major and trace element concentra- tions in humic acid. We used and compared the results each other of three independent analytical techniques as prompt-gamma activation analysis (PGAA), neutron ac- tivation analysis (NAA) and X-ray fluorescence (XRF).

## 2 Sample

The investigated humic acid originates from the Carpathian Basin, close to the village of Nagyvázsony, Hungary. The probes were manufactured by Gy. Pádi from lignite according to a Hungarian National Patent, see Ref. [14]. The material itself is a gray powder with very low solubility even in strong acids and alkalis.

## 3 Materials and methods

A humic acid sample was analyzed with neutron activation (NAA) and prompt-gamma activation (PGAA) analytical methods. The measurements were performed at the Budapest Neutron Centre (BNC) [15]. 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 [16]. 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 applied. The measurements were performed in the Environmental Physics Laboratory at the Centre for Energy Research, Hungarian Academy of Sciences.

**Comment [NF1]:** The topic can be changed like " Evaluation of major and trace elements present in extracted humic acid from lignite coal"
Or "Extraction and Characterization of major and trace elements from humic acid sample of Hungary"

**Comment [NF2]:** Abstract is not upto the mark. It must include some back ground of study in 2 lines+ techniques used+ some findings or major results of the study.

**Comment [NF9]:** Mention the depth and location of coal sample briefly.

**Comment [NF3]:** This line must be changed . It seems to be vague.

**Comment [NF4]:** The researcher

**Comment [NF5]:** elemental

**Comment [NF6]:** there is no analytical data

**Comment [NF7]:** research

**Comment [NF8]:** introduction portion need to add some more up to date information and some brief description of humic acid.

**Comment [NF10]:** Was also applied

### 3.1 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 µg/g concentration range or below. NAA method requires only simple sample preparation. For the measurement only a small amount of sample is needed, however, the irradiated samples become radioactive, therefore they cannot be returned to the owner.

For $k_0$-NAA irradiation, 108 µg humic acid powder sample was heat-sealed in high-purity quartz ampule (Suprasil AN, Heraeus). The quartz ampule was wrapped in aluminum foil and it was 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 (‼.17) has been 1.86· $10^{13}$ cm$^2$ s$^{-1}$. Prior to the gamma counting, the irradiated quartz vial was 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 sample were counted within low-level counting chamber (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 × 16 k channel were recorded with the zero-dead time (ZDT) option to accurately account for the different time dynamics of the isotopes [17]. The corrected and uncorrected halves of the spectra are stored in a single SPC file. For spectrum evaluation HyperLab 2013.1 software was used [18]. For identification of radioactive isotopes and for element concentration calculations KayZero for Windows 3.06 program [19] 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 [20].

### 3.2 PGAA

Prompt gamma activation analysis is also a nuclear analytical technique for non-destructive determination of elemental and isotopic compositions [23]. 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.

**Comment [NF11]:** Is it reference 21 or the reference 21 is missing???

For PGAA analysis, 6 g-portion was weighed and heat-sealed into Teflon bags. The neutron flux at the sample position of the PGAA station was about 9.6 $10^7$ cm$^2$ s$^{-1}$. The cross-section of the neutron beam was adjusted to 20 × 20 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 has been described in details in an earlier publication [22]. 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 [23].

### 3.3 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$\alpha$ 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 [24]. 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 [25].

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.

**Comment [NF12]:** These lines need some clarification. I am unable to understand what exactly author wants to mention.

| | | PGAA | | NAA | | XRF | | $\frac{c(NAA)}{c(PGAA)}$ | $\frac{c(XRF)}{c(PGAA)}$ | $\frac{c(XRF)}{c(NAA)}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Z | El | $c\,[\mu g/g]$ | $\delta c\,[\%]$ | $c\,[\mu g/g]$ | $\delta c\,[\%]$ | $c\,[\mu g/g]$ | $\delta c\,[\%]$ | | | |
| 1 | H | 38200 ± 1973 | 5.17 | | | | | | | |
| 5 | B | 77.60 ± 4.03 | 5.19 | | | | | | | |
| 6 | C | 354400 ± 19059 | 5.38 | | | | | | | |
| 8 | O | 478300 ± 23902 | 5.00 | | | | | | | |
| 11 | Na | 1150 ± 46 | 4.00 | 979.00 ± 17.88 | 1.83 | | | 0.85 | | |
| 12 | Mg | 4790 ± 388 | 8.11 | | | | | | | |
| 13 | Al | 9570 ± 566 | 5.92 | | | | | | | |
| 14 | Si | 39100 ± 2232 | 5.71 | | | | | | | |
| 16 | S | 29600 ± 1640 | 5.54 | | | 5240 ± 700 | 13.36 | | 0.18 | |
| 17 | Cl | 221.00 ± 12.15 | 5.50 | | | | | | | |
| 19 | K | 2610 ± 145 | 5.58 | 2440 ± 80 | 3.30 | 1340 ± 160. | 11.94 | 0.93 | 0.51 | 0.55 |
| 20 | Ca | 36400 ± 2194 | 6.03 | 35170 ± 2618 | 7.44 | 33800 ± 630 | 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 ± 335 | 5.70 | 5739 ± 111 | 1.93 | 3760 ± 32 | 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 | | | 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 | | | | | | | |
| 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 threee measurements

**Comment [NF13]:** Spellings need to be correct + the caption of table must be mentioned above the table.

## 4 Results and discussion

In this section we present and compare the quantitative results obtained from the analysis of different spectra measured with NAA, PGAA and XRF methods, respectively.

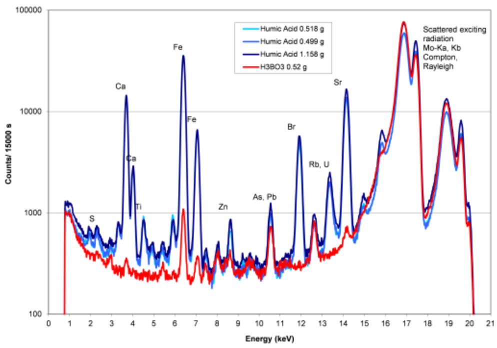

**Fig. 1.** X-ray spectra collected from humic acid pellets of 0.5-1.1 g compared to a blank X-ray spectrum of 0.5 g boric acid.

We summarize our experimental data in Table 1. We present the measured concentrations with the systematic errors, and the three ratios.

Using NAA technique, 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%. (See Table 1.) The elemental concentrations are given in μg/g SI units, with absolute (μg/g) and relative (%) uncertainty. It is clear that this method identifies the largest number of trace elements.

Table 1 also contains the concentrations of the major elements (in oxide and elemental form in wt%), and the trace elements (in μg/g) together with their relative $2\sigma$ ($k = 2$) uncertainties measured by PGAA. 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.

Using XRF, concentrations of 17 minor and trace elements could be determined. The presence of Br at elevated concentration in the humic acid samples is clearly visible in the X-ray spectra (Fig. 1.), 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.

## 4 Summary and conclusions

We presented a comparative study of the major and trace element spectra of humic acid. Three different element analytical methods, NAA, PGAA and XRF were used. 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. are measured which of soil conditioners. We identified 42 different elements. Further work is in progress, we plan to analyze our humic acid sample with additional spectroscopic methods like Raman or Mössbauer spectroscopy.

Table 1 shows one of the main advantages of the PGAA method; it is capable of measuring the concentration of light elements (including Hydrogen) non-destructively. The PGAA and NAA results show quite good agreement. Moreover, Table 1 shows the complementary character of the two methods above.

The XRF results show tendentiously lower values compared to that of the PGAA and NAA. A possible explanation could be the lower penetration depth of the X-rays into matter compared to that of neutrons because some inhomogeneities in the sample could cause different results.

## 5 Acknowledgment

The ELI-ALPS project (GINOP-2.3.6-15-2015-00001) is supported by the European Union and co-financed by the European Regional Development Fund. One of us K. Tőkési acknowledges the support by the National Research, Development and Innovation Office (NKFIH), Grant No. KH 123886.

## References

1. J.S. Gaffner, N.A. Marley and S.B. Clark, *Humic and Fulvic Acids,* ACS Symposium Series; American Chemical Society: Washington, DC, 1996.
2. E. A. Ghabbour and G. Davie, *Humic Substances Structures, Models and Functions* , Published by The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 OW, UK Registered Charity No. 207890, 2001.
3. G.R. Aiken, D. M. McKnight, R.L. Wershaw and P. Maccarthy, *Humic Substances in Soil, Sediment and Water* A Wiley Interscience Publication, John Wiley & Sons, 1985.
4. N. Belize, H.A. Joly and H. Li, Can. J. Chem. **75,** (1997) 14.
5. D. Dudare, O. Purmalis and M. Klavins, Environment. Technology. Resources Proceedings of the 8th International Scientific and Practical Conference. Volume 1 Rezeknes Augstskola, Rezekne, RA Izdevnieciba, 2011.
6. F. de Souza and S. R. Braganc, J. Mater. Res. Technol. **6,** (2017) 157.
7. M. Giovanella, E. Parlanti, E. J. Soriano-Sierra, M. S. Soldi and M. M. D. Sierrra, Geochemical Journal, **38,** (2004) 255.
8. B.A.G. de Melo, F.L. Motta, M.H.A. Santana, Materials Science and Engineering C **62,** (2016) 967.
9. Aly A. Helal, G.A. Murad and A.A. Helal, Arabian Journal of Chemistry, **4,** (2011) 51.
10. J.A. Rice and P. McCarthy, Org. Geochem, **17,** (1991) 635.
11. Z. Shuiquin, Y. Liang, L. Wei, L. Zhian, L. Yanting, H. Shuwen and Z. Bingqiang, Chemosphere **166,** (2017) 334.
12. H. Mengchang, S. Yehong and L. Chunye, Journal of Environmental Sciences **20,** (2008) 1294.
13. M.P. Sartakov, N.V. Shpynova, I.D. Komissarov and Yu. M. Deryabina, International Journal of Green Pharmacy **11,**

COMPETING INTERESTS DISCLAIMER:
Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

**Comment [NF14]:** I propose to list some discussion with other researcher findings in order to make results more captivative and elaborated.

**Comment [NF15]:** The conclusions, however, I think should be presented more extensively and in an orderly manner. The partial conclusions obtained should be detailed, as well as the final conclusion that can be drawn from this research. This section should be modified

14. E. Dudás, Gy. Pádi, M. Ürmossy, B. Toth, Á. Nemes and L. Simon, *Hungarian Patent Nr.182147,* “Eljaras természetes eredetű szerves anyagok oxidativ előkezelésére”, dated 1987. VI. 15.
15. Budapest Neutron Center, www.bnc.hu.
16. K. Gmling, A. Simonits, I. Sziklai-László, D. Párkányi, J. Radioanal. Nucl. Chem. **300,** (2014) 507.
17. L. Szentmiklósi, D. Párkanyi and I. Sziklai-László, J. Radioanal. Nucl. Chem. **309,** (2016) 91.
18. A. Simonits, J. Ostor, S. Kalvin *et al.,* J. Radioanal. Nucl. Chem. **257,** (2003) 589.
19. F. De Corte, R. van Sluijs, A. Simonits *et al.,* Appl. Radiat Isot **55,** (2001) 347.
20. F. De Corte F and A. Simonits, At. Data Nucl. Data Tables **85,** (2003) 47.
21. Zs. Révay and T. Belgya, Principles of the PGAA method. In: Molnr, G.L. (Eds.), *Handbook of Prompt Gamma Activation Analysis with Neutron Beams* Kluwer, pp. 1-30. (2004).
22. L. Szentmiklósi, T. Belgya, Zs. Révay and Z. Kis, J. Radioanal. Nucl. Chem. **286,** (2010) 501.
23. Zs. Révay, R.B. Firestone, T. Belgya and G.L. Molnár, *Catalog and Atlas of Prompt Gamma Rays in Handbook of Prompt Gamma Activation Analysis with Neutron Beams,* ed. G.L. Molnár, Kluwer Academic Publishers, Dordrecht/Boston/New York, (2004) 173364.
24. B. Vekemans, K. Janssens, L. Vincze, F. Adams and P. Van Espen, X-Ray Spectrom. **23,** (1994) 278.
25. J. Osán, S. Kurunczi, S. Torok and R. Van Grieken, Spectrochim. Acta Part B **57,** (2002) 413.

**Comment [NF16]:** Need to add some up to date references.