

STUDIES TO DETERMINE WHETHER UNDERGROUND WATERS IN WIELKOPOLSKA REGION (POLAND) CONTAINING HUMUS SUBSTANCES ARE SUITABLE FOR PRACTICAL PURPOSES

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ABSTRACT

Background. Water derived from Miocene aquifer in Wielkopolska region (Poland) has a 'brown-black' colouration resulting from humus substances. Because this colour is difficult to remove, such water is considered unfit for human consumption. The presence of naturally occurring humus acids with known biochemical properties may however lend such water for use in medicine, cosmetics or agriculture.

Objective. To determine and evaluate the properties of 'brown-black' Miocene waters from analysing their physico-chemistry properties, mineral content and the presence and structures of humus acids.

Material and Methods. The test material was 4 samples of intensely coloured 'brown-black' underground waters from Miocene aquifer taken from the Greater Poland region at different locations; Obrzycko and Braczewo (both by Szamotuly), Sepno (by Koscian) and in Poznan (Szkolna Street).

Results. The water type was $\text{HCO}_3\text{-Cl-Na}$ with dissolved minerals ranging at concentrations of 828.5 mg/dm^3 (Poznan) to 1600.5 mg/dm^3 (Obrzycko). Fluorides were present at 0.71 mg/dm^3 (Poznan) to 1.41 mg/dm^3 (Braczewo) whilst iron (II) (ferrous ion) ranged from >10 mg/dm^3 (Obrzycko) to 22.7 mg/dm^3 (Sepno). Levels of humus acids varied between 188.6 mg/dm^3 (Sepno) to 1501.8 mg/dm^3 (Obrzycko) with predomination humic acids over hylatomelanic acids by factors from 1.3 to 10.6.

Conclusions. Due to the test water's mineral content, which includes significant levels of iron II, fluoride and humus acids (> 50 mg/dm^3), it is suggested that it has therapeutic value and is suitable for medicinal bath treatments and in manufacturing medical products or cosmetics.

Key words: *miocene water; specific humus therapeutic water; humus substances; differential absorption spectra UV/VIS*

STRESZCZENIE

Wprowadzenie. Na terenie Wielkopolski w utworach miocenu występują wody "brunatno-czarne", których barwa pochodzi od związków humusowych. Wody te, ze względu na trudności w usuwaniu zabarwienia uznawane są za nieprzydatne do zaopatrywania ludności. Obecność kwasów humusowych naturalnego pochodzenia o udokumentowanych badaniami właściwościach biochemicznych, może determinować racjonalne wykorzystanie takich wód, m.in. do celów leczniczych, kosmetycznych czy rolniczych.

Cel. Celem opracowania było rozpoznanie i ocena właściwości „brunatno-czarnych” wód poziomu mioceńskiego na podstawie wyników analiz: fizyko-chemicznych, składu mineralnego oraz zawartości i struktury kwasów humusowych.

Material i metody. Materiałem do badań były wody podziemne „brunatno-czarne” z mioceńskich warstw wodonośnych, pochodzące z 4 ujęć na terenie Wielkopolski w miejscowościach: Obrzycko i Braczewo – k/Szamotuł, Sepno – k/Kościana oraz w Poznaniu – (ul. Szkolna), charakteryzujące się intensywną barwą i klarownością.

Wyniki. Badane „brunatno-czarne” wody z terenu Wielkopolski są wodami typu $\text{HCO}_3\text{-Cl-Na}$ zawierającymi od 828,5 mg/dm^3 (Poznań) do 1600,5 mg/dm^3 (Obrzycko) rozpuszczonych składników mineralnych. W wodach tych obecne są fluorki w stężeniu: od 0,71 mg/dm^3 (Poznań) do 1,41 mg/dm^3 (Braczewo) oraz w 2 ujęciach (Obrzycko, Sepno) żelazo (II) w stężeniu > 10 mg/dm^3 (do 22,7 mg/dm^3). Badane wody zawierają w przedziale stężeń od 188,6 mg/dm^3 (Sepno) do 1501,8 mg/dm^3 (Obrzycko) kwasy humusowe, w których przeważają kwasy huminowe nad hylatomelanowymi w stosunku od 1,3 do 10,6.

Wnioski. Ze względu na skład mineralny, w tym znaczącą zawartość żelaza (II) i fluorków a także zawartość kwasów humusowych w stężeniu > 50 mg/dm^3 , proponuje się badane wody uznać jako swoiste lecznicze wody humusowe oraz wykorzystać je do celów leczniczych w formie kąpeli oraz do produkcji preparatów leczniczych czy kosmetycznych.

Słowa kluczowe: *woda mioceńska, swoista lecznicza woda humusowa, związki humusowe, różniczkowe widmo absorpcji UV-VIS*

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INTRODUCTION

The underground water from the Miocene aquifer found throughout the Polish lowlands, (particularly the Greater Poland region), is intensively coloured 'brown-black' ($>120\text{-}28000\text{ mgPt/dm}^3$). Historically, it had been used for generating steam in steam engines, in filling fire extinguishers or for industry as water in heat exchangers, but rarely for agriculture [11, 12, 15]. However, because of the high treatment costs this water is uneconomical for human consumption as for example as drinking water. The water's discolouration is due to humus compounds, mainly humic acids, which are particularly present in peat, lignite and soil as well as some surface waters. In peat treatments, these substances form a significant part of the organic component. Their large presence arises from their biochemical properties [10, 13, 18] and as such, constitute the treatment's active ingredients because of their antioxidant, antibacterial and astringent actions along with physicochemical properties of adsorption, complexation and ion exchange. Fulvic, humatomelanic and humic acids are the main humus substances that are bioavailable and bioactive at their appropriate concentrations and chemical form, particularly if soluble [6]. Studies have shown that water is a natural solvent for humus substances as well as those linked to minerals. Early work on the pharmacodynamics and chemistry of Miocene water from Braczewo [1, 2] has indicated the potential for exploiting the biochemical properties of such water.

The study aim was to thus determine the composition of minerals and organic material in chosen 'brown-black' water samples obtained from Miocene aquifer waters and evaluate the results according to criteria set/judged for waters to be therapeutic [20].

MATERIALS AND METHODS

Subject material were 4 samples of 'brown-black' underground waters from Miocene aquifer taken at different locations in the Greater Poland region; Obrzycko and Braczewo (both by Szamotuly), Sepno (by Koscian) and in Poznan (Szkolna Street). Subsequent analyses consisted of determining the following;

- Physicochemical and organoleptic properties.
- The contents of basic minerals, specific therapeutic

substances and humus acids which included humic, fulvic and humatomelanic acids along with total organic carbon.

Where the following analytical techniques were employed;

- A multifunctional CX-701 (Elmetron) electro-metric analyser using a PT-100 temperature sensor (Elmetron) and electrodes for the following measurements: pH (ERH-Hydromet), electric conductivity (EC-60-Elmerton), redox potential (EPtAgP-323W-Eurosensor), fluoride (ion selective fluoride Orion 9609BNWP-Thermo) and iodides using an ion selective iodide-(Detektor) electrode of the RL-100 -Hydromet.
- Spectrophotometry (U-1800-Hitachi) for determining colour, iron, metasilicic acid and absorbances at A_{465} , A_{665} .
- Total organic carbon (TOC) using the TOC-V_{CSH} (Shimadzu) analyser.
- Sodium and potassium by the BWB-XP 2011 flame photometer.
- Gravimetric method for measuring sulphates and humus acids (after precipitation and drying).
- Complexometric titration for determining calcium, magnesium, argentometric titration for chloride and acidimetric titration for bicarbonate.

From the test samples, humus acid fractions of fulvic acid, humic acid and humatomelanic acid were first isolated by selective solvent extraction (acid, alcohol, base) followed by obtaining their spectra between 200-800 nm. The precise extraction procedure and spectrophotometry are detailed elsewhere [2], where for the latter, quartz cuvettes were used at a path length of 1cm and scan rate of 800nm/min. The spectra were then subjected to Savitsky-Golay spectral smoothing followed by 4th derivative numerical differentiation. Specific humus acids were identified by their absorption peaks from a comparison with humus acid standards (from Fluka) at a concentration of 1g/dm³ [7].

RESULTS AND DISCUSSION

The basic physico-chemical and organoleptic properties of test samples are presented in Table 1 (ie. colour, redox potential, pH, conductivity and absorbance at 465 and 665 nm).

Table 1. Some physico-chemical features of the tested miocene waters

Water source	Colour [mg Pt/dm ³]	Redox potential [mV]	pH	Conductivity [$\mu\text{S/cm}$]	Absorbance (λ)	
					465 nm	665 nm
Obrzycko	28 000	- 142.5	7.70	1986	3.399	0.928
Braczewo	3 500	- 126.6	7.49	1863	1.667	0.394
Sepno	3 500	- 231.7	7.33	810	1.042	0.267
Poznan	4 100	- 84.9	7.31	1024	1.485	0.365

The hydro-geochemical redox potential (E_h) conditions prevailing in the Miocene water aquifer were found to be reducing and ranged from 7.0 (Sepno) to 11.8 (Poznan), [16]. An indicator of humification has been taken as the absorbance ratio A_{465}/A_{665} [14, 17] and was determined as being 3.66 (Obrzycko), 4.23 (Braczewo), 4.08 (Poznan) and 3.90 (Sepno). Ratio

values < 5 are considered to show that the aromatic centres of humus acids therein have a high degree of condensation, with cyclic structures predominating over aliphatic chains [3, 4, 19, 21].

Table 2 shows the cationic and anionic contents, as well as other the specific therapeutic compounds.

Table 2. Test water content of cations, anions and specific therapeutic compounds.

Water source	Cations and anions							Specific therapeutic compounds			
	Concentration [mg/dm ³]							Fe ^{2+/3+}	F ⁻	I ⁻	H ₂ SiO ₃
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻				
Obrzycko	408.2	7.14	71.1	7.90	452.0	617.5	< 1.0	22.71	1.32	0.08	12.5
Braczewo	406.5	6.14	27.1	9.11	407.7	520.8	< 1.0	2.15	1.41	0.09	14.2
Sepno	242.5	5.02	29.1	11.5	214.8	451.0	< 1.0	13.02	1.36	0.08	11.2
Poznan	188.9	5.11	43.2	10.9	241.0	311.4	< 1.0	2.85	0.71	0.09	23.6

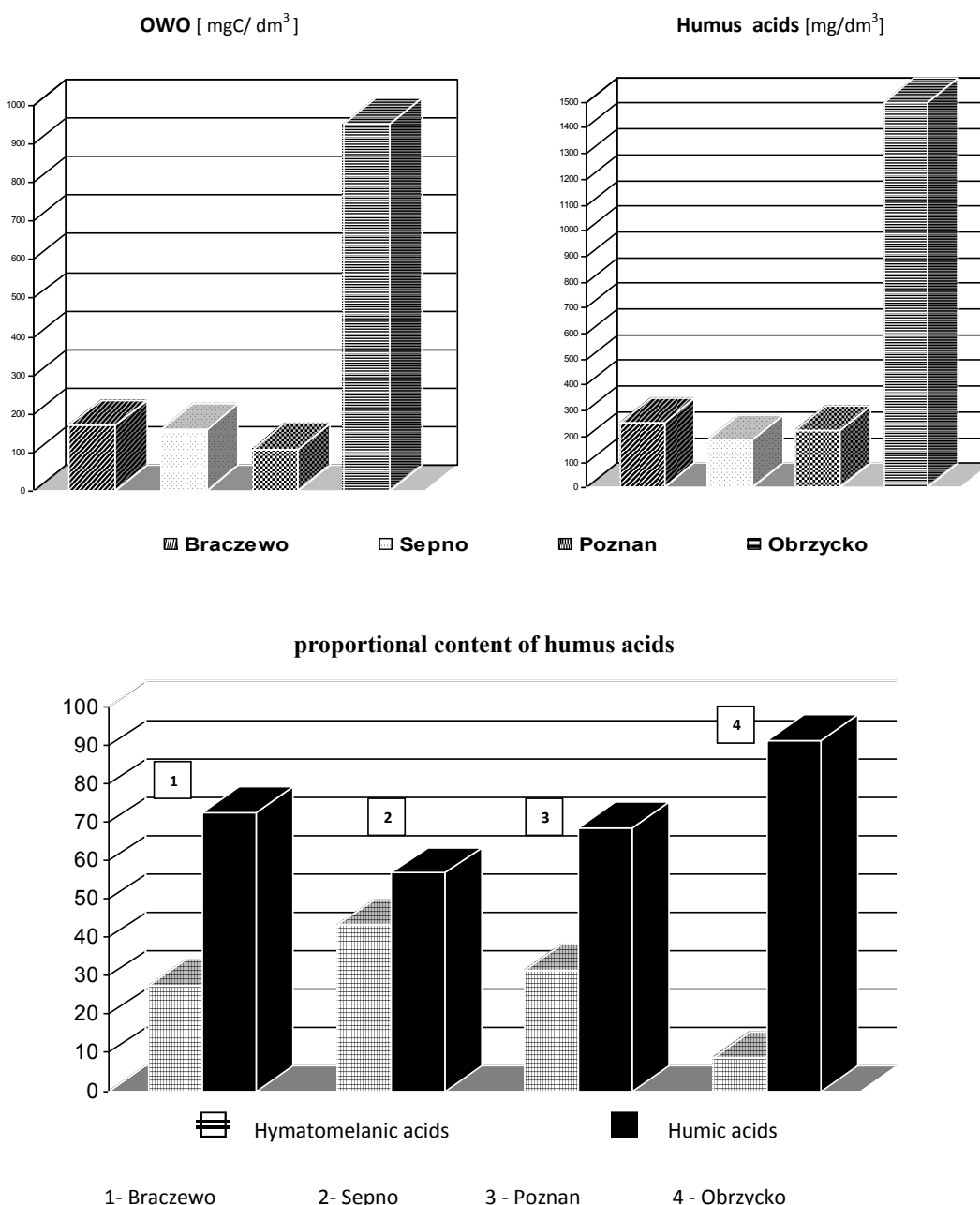


Figure 1. The proportional TOC content and content of humus acids divided into their respective fractions (hymatomelanic acid, humic acid) in test waters

The tested water was found to belong to the HCO_3^- -Cl-Na type with levels of minerals in general being 0.16% (Obrzycko), 0.14% (Braczewo), 0.10% (Sepno) and 0.08% (Poznan). Of the other specific therapeutic compounds, fluoride had the highest concentrations, ranging from 0.71 mg/dm^3 (Poznan) to 1.41 mg/dm^3 (Braczewo) but was below the 2 mg/dm^3 limit. Significant amounts of iron (II) were found in Obrzycko

(22.7 mg/dm^3) and Sepno (13.0 mg/dm^3) compared to therapeutic standard levels of 10.0 mg/dm^3 . Iodide concentrations lay between 0.08 to 0.09 mg/dm^3 . The content of humus acids divided into their respective fractions (hymatomelanic acids, humic acids and TOC) are presented in Figure 1.

Humus acids were measured as being between 188.6 mg/dm^3 (Sepno) to 1501.8 mg/dm^3 (Obrzycko). All samples

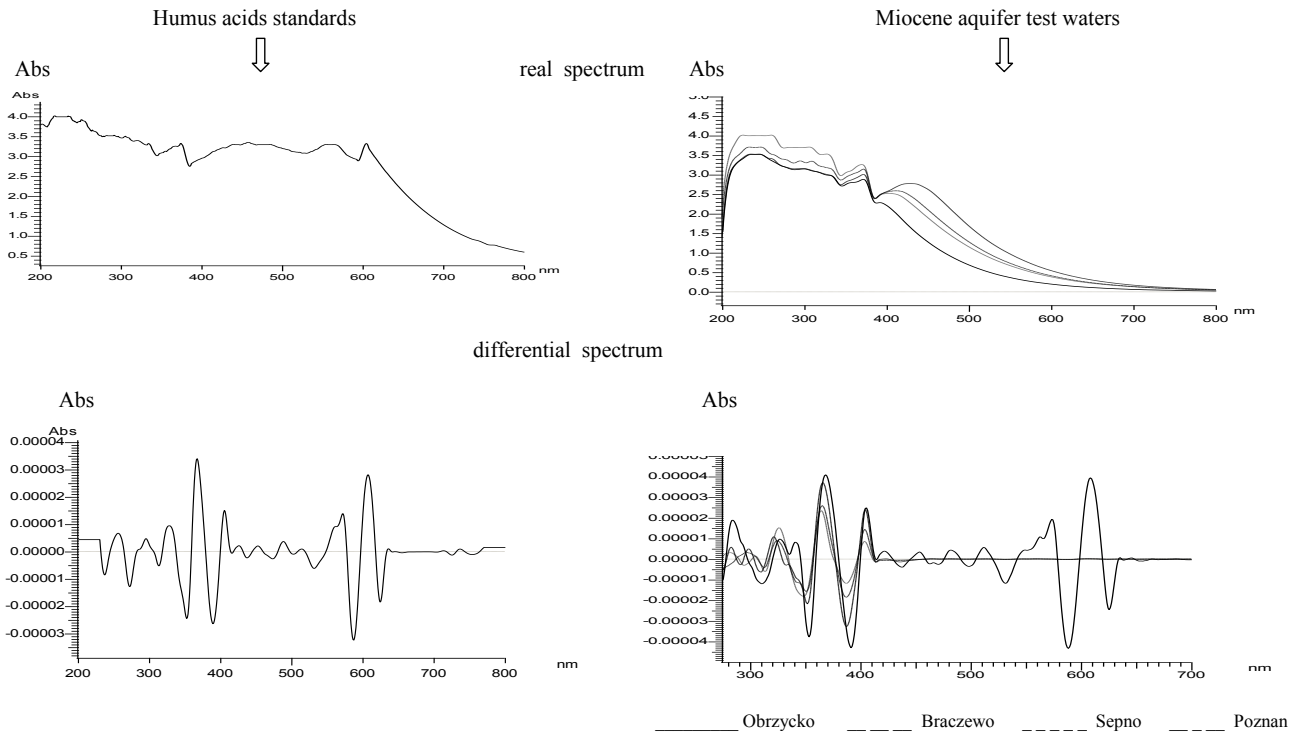


Figure 2. Real and differential absorptive spectra of humus acids standards and brown-black humus waters

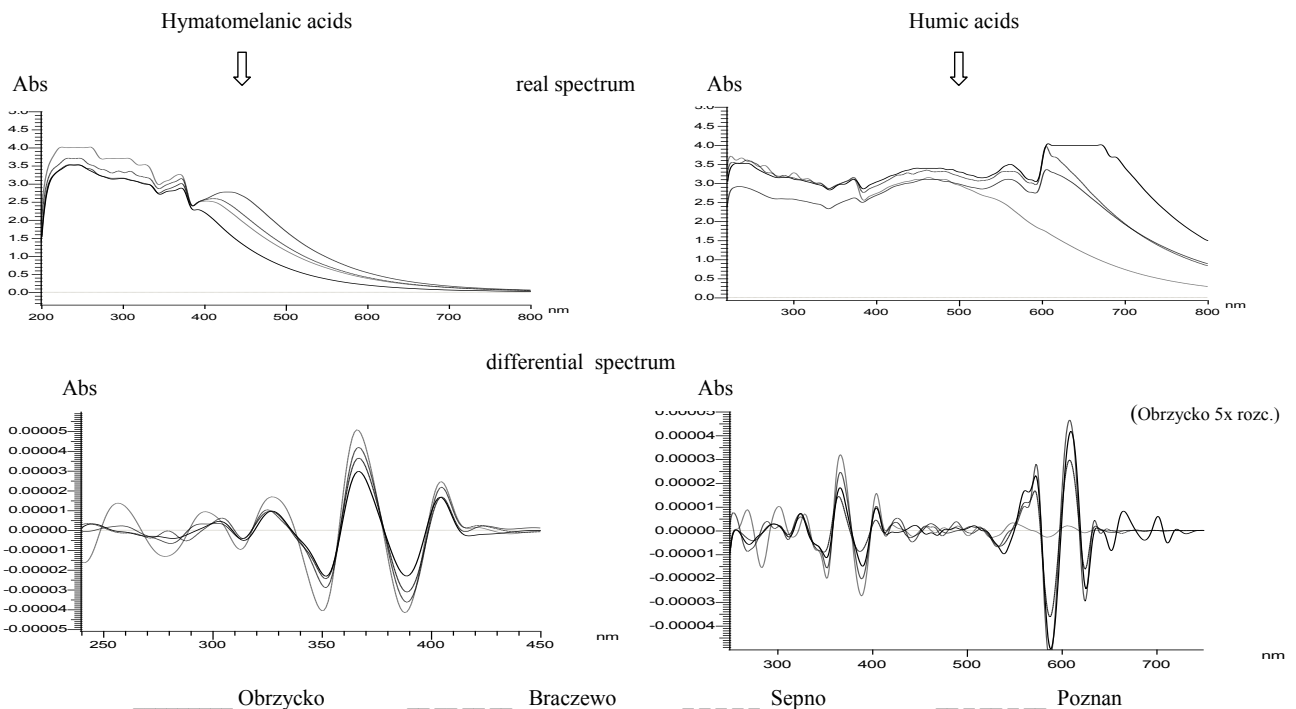


Figure 3. Real and differential absorptive spectra of hymatomelanic and humic acids isolated from Miocene aquifer test waters

demonstrated a clear predominance of humic acids over humatmelanic acids ranging from 1.3-fold in Sepno to 10.6-fold in Obrzycko. Fulvic acids were however absent.

Real and differentiated absorption spectra for humus acid standards are presented in Figure 2, whilst those for humus acids isolated are shown in Figure 3.

It was found that the absorption spectra for 'brown-black' waters are similar to the humus acid standards and to those substances present in peat [5, 7]. These similarities are first evident in the curve shape of actual spectra, with absorbance decreasing monotonically with increasing wavelength around from the transition area between the UV to the visible range. Secondly in the differentiated spectra, where the absorption peaks characteristic of specific humus acids were in both cases similar. Furthermore, when the test waters were heated to 80 °C there was no precipitation observed (including any of the humus acids).

In summing up it should be noted that our earlier studies touted the possibility of using some Miocene waters for Health-Spa baths in conjunction with waters containing sulphides and bisulphates. Their use in manufacturing cosmetics containing humus acids was also considered [9].

CONCLUSIONS

1. Sampled underground test waters from Poznan, Sepno, Obrzycko and Braczewo have a chemical composition that indicate a use in balneotherapy (mainly through mineral baths and body cavity irrigation) as well as in cosmetics and agriculture
2. Findings could be used to support an additional type of classification for therapeutic waters; a novel kind which contains at least 50 mg/dm³ of humus acids.

Conflict of interest

The authors declare no conflict of interest.

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lenia właściwości leczniczych naturalnych surowców leczniczych właściwości leczniczych klimatu, kryteriów ich oceny oraz wzoru świadectwa potwierdzającego te właściwości (Dz. U. Nr 80 poz. 565).

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