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THE ELEMENTS OF SPECIFIC BIOLOGICAL ACTIVITY IN THERAPEUTIC WATERS IN POLISH HEALTH RESORTS

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Abstract

The study characterizes specific therapeutic waters in Polish health resorts, which contain iodide, fluoride, silicon, sulphides, iron(II), carbon dioxide and radon in concentrations that ensure the therapeutic status of water and specify how it can be used for medical treatment.

Based on the physicochemical analysis, it has been verified that among 160 waters from 39 health resorts, 37 contain Fe(II) in concentrations > 10 mg dm^{-3}, which means that they can be classified as ferruginous. Twelve waters containing fluoride in concentrations > 2 mg dm^{-3} were recognized as therapeutic fluoride waters. Five waters were classified as siliceous ones owing to the content of silicon compounds above 70 mg dm^{-3} (H_2SiO_3). Twenty-eight of the analysed waters contain sulphides (H_2S+HS^-) in concentrations > 1 mg dm^{-3} and 64 waters contain iodide in concentrations > 1 mg dm^{-3}. Carbon dioxide, which occurs in 72 waters in concentrations above 1 g dm^{-3} (acidulous waters), proved to be the most widespread component. Waters which contain radon in an amount corresponding to the radiation of 74 Bq (2 nCi) in 1 dm^3 are classified as radon waters. Ten of the analysed waters were found to contain this element.

The waters were highly varied in chemical composition and type of specific components. Sulphurous waters are mainly used for mineral baths; ferruginous waters are drunk; fluoride and silicon-rich waters are taken for mineral baths and iodide waters are used for mineral baths and inhalations. Using these waters in balneotherapy is an important part of spa treatment and defines different healing profiles of Polish health resorts.

Key words: specific therapeutic waters, sulphides, iodides, fluorides, iron (II), silicon, radon, carbon dioxide.

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PIERWIASTKI O SWOISTEJ AKTYWNOŚCI BIOLOGICZNEJ W WODACH LECZNICZYCH POLSKICH UZDROWISK

Abstrakt

W pracy przedstawiono charakterystykę leczniczych wód swoistych polskich uzdrowisk. Są to wody zawierające jodki, fluorki, związki krzemu, związki siarki (II), żelazo (II), dwutlenek węgla i radon w stężeniach decydujących o statusie leczniczym wody i sposobie jej wykorzystania do zabiegów kuracyjnych.

Na podstawie wyników analiz fizykochemicznych stwierdzono, że spośród 160 wód pochodzących z 39 miejscowości uzdrowiskowych 37 wód zawiera żelazo (II) w stężeniu > 10 mg dm^{-3} wymaganym dla uznania wody za żelazistą; 12 wód zawierających fluorki w stężeniu > 2 mg dm^{-3} uznano za lecznicze wody fluorkowe; 5 wód ze względu na zawartość związków krzemu w stężeniu > 70 mg dm^{-3} (H_2SiO_3) zaliczono do wód krzemowych; 28 wód zawiera związki siarki (II) w stężeniu > 1 mg dm^{-3} ($HS^- + H_2S$), a 64 wody zawierają jodki w stężeniu > 1 mg dm^{-3}. Najczęściej występującym składnikiem swoistym wód leczniczych jest dwutlenek węgla, którego stężenie w 72 wodach przekracza 1 g dm^{-3} (szczawy). Wody zawierające radon w ilości, której odpowiada aktywność promieniotwórcza co najmniej 74 Bq dm^{-3} (2 nCi), są zaliczane do wód radonowych. Pierwiastek ten występuje w 10 badanych wodach.

Omawiane wody charakteryzują się dużym zróżnicowaniem podstawowego składu chemicznego oraz zawartością ww. składników swoistych. Wody swoiste siarczkowe są wykorzystywane głównie do kąpieli, wody żelaziste do kuracji pitnych, wody fluorkowe i krzemowe do kąpieli, a jodkowe do kąpieli i inhalacji. Stosowanie tych wód w balneoterapii stanowi ważną część działalności uzdrowiskowej i uzasadnia różne profile lecznicze polskich uzdrowisk.

Słowa kluczowe: swoiste wody lecznicze, związki siarki (II), jodki, fluorki, żelazo (II), krzem, radon, dwutlenek węgla.

INTRODUCTION

In the literature dealing with balneology and in spa practice, the following elements have significant influence on the human body: macroelements (sodium, potassium, calcium, chlorides, bicarbonates, sulphurs) and specific components (iodides, compounds with sulphur(II), silicon, fluorine, iron(II) and radon as well as carbon dioxide). In some waters, concentration of these components determines their therapeutic properties and specifies the type of treatment, e.g. drinking water, mineral baths or inhalation therapy. The minimum concentration of these components for healing applications is set in the Regulation of the Minister for Health of 13 April 2006 (Journal of Law, 2006.80.565).

The aim of the study has been to demonstrate some characteristics of the therapeutic properties of specific waters containing sulphlides, iodides, fluorides, iron, silicon, radon and carbon dioxide, which occur in some of the Polish spas and which are currently used.

MATERIAL AND METHODS

This review is based on the authors' own results of physical and chemical analyses of spa waters, which were performed during the certification of spa waters in 2007-2010. The results from the previous years, 1998 to 2006, originate from own analyses as well as from data supplied by other institutions authorized to analyse water.

The composition of 160 waters from 39 spas in four regions of Poland, i.e. the Carpathian Mountains, an area of Miocene marine sediments, the Sudety mountains and the Polish Lowland, was analyzed.

RESULTS AND DISCUSSION

Acidulous waters (over 1 g dm^{-3} CO_2) and waters containing carbon dioxide

The most common component of specific water is carbon dioxide, which occurs in 88 of all the analysed healing waters from the south of Poland. In 16, the concentration of CO_2 was 250-1.000 mg dm^{-3} (waters containing carbon dioxide) and in 72, the concentration was above 1.0 g dm^{-3}, which means that they belong to acidulous waters. The concentration of CO_2 in such water can reach 3,316 mg dm^{-3} (intake Zofia II in Żegiestów), but is normally in the range from 2,800 to 2,970 mg dm^{-3}, especially in the intakes in Wysowa and Krynica. Carbon dioxide usually occurs in the water types: HCO_3-Cl-Na/Ca, I (Rymanów, Wysowa, Szczawnica, Rabka, Kudowa); HCO_3-Ca-Mg, HCO_3-Ca (Muszyna, Krynica); HCO_3-Na (Krynica, Szczawno), and in low mineralized ferruginous and radon waters (Świeradów, Lądek). In balneochemistry, when characterising mineral water, names of dominant anions and cations are given in the order of decreasing concentrations. Concentration is expressed in milligram-equivalent per 1 dm^3.

Carbon dioxide is a natural stabilizer of mineral water composition. It maintains carbonic acid and solubility balance, thereby preserving bio-accessible forms of chemical compounds of calcium, magnesium, iron and manganese. This is very important when acidulous waters are used for drinking treatment, which is the main application of these waters.

It is less popular to use acidulous waters for mineral baths due to their limited resources. However, there are clinical observations confirming good localised effect as well as positive influence of carbon dioxide on the human body during a bath, as a result of the release of tissue hormones in the skin, expansion of capillaries, decreased heart rhythm, lowered blood pressure, improved diuresis, accelerated metabolism and improved blood rheology (Drobnik, Latour 2001, 2002, 2006, Gutenbrunner 1990). At present, the

acidulous waters available in Polish health resorts are not available as bottled water to continue treatment outside a spa.

Ferruginous waters

There are 42 iron water intakes in 15 Polish spas which have water with at least 10 mg dm^{-3} of iron(II); this is the threshold level to assume that they are ferruginous waters. The highest concentration of iron(II) in the range from 217.7 to 270.0 mg dm^{-3} was found in the intakes in Świeradów and Wysowa; in the area of Krynica-Żegiestów, Kudowa, Goczałkowice and Świnoujście, it ranged from 47.5 to 95.1 mg dm^{-3} and in Konstancin, Busko, Świeradów and Wysowa, it varied from 20 to 40 mg dm^{-3}. Iron(II) usually occurs in the following water types: Na-Cl (brine with the general mineral content higher than 1.5%), (11 intakes), acidulous waters –HCO_3--Mg-Ca (8 intakes); – HCO_3-Na-Ca (6 intakes); –Cl-Na (4 intakes), all characterised by a different level of mineralization. Many ferruginous waters contain other specific components, mainly iodides and carbon dioxide.

Iron (II) in essential for haemoglobin production. It also has positive influence on the growth and development of muscles, as well as the formation and activity of enzymes which control the heart and improve the immune system (REINHOLD 1995).

When formulating therapeutic recommendations for waters containing iron(II), it is important to consider the general mineralization of water and concentration of other components. Iron in mineral water can have a medicinal effect only when administered *per os*. Consequently, the best results can be achieved by drinking such waters as acidulous waters HCO_3-Mg-Ca, HCO_3-Na-Ca, low mineralized waters, mineralized waters and Cl-Na with mineralization lower than 0.9%.

Iron occurs in many brine waters used for mineral baths (in significant concentrations, e.g. in Goczałkowice, Świnoujście), but then it does not have any influence on the human body.

Iodide waters

Waters from 61 intakes in 17 spas have been classified as iodide waters, containing at least 1.0 mg I^- dm^{-3}. Iodides in concentrations above 10 mg dm^{-3} occur in 2 intakes in Busko, 2 intakes in Iwonicz, 1 intake in Ustroń, and in all the intakes in Rabka (5 intakes) and Goczałkowice (3 intakes). The highest iodide concentration was found in Ustroń (31.9 mg I^- dm^{-3}), Goczałkowice (19.0-22.2 mg dm^{-3}) and Rabka (12.9-21.2 mg dm^{-3}). Iodide waters are generally Cl-Na waters (also brine), Cl-SO_4-Na waters, and carbonated waters or acidulous waters Cl-HCO_3-Na (low and medium mineralized).

Iodides produce various effects on the human body, depending on the type of treatment. Iodides from Cl-SO_4-Na waters (Busko), waters containing carbon dioxide or acidulous waters like Cl-HCO_3-Na (Iwonicz) used as drinking water affect production of the thyroid hormones and metabolism. Iodides from Cl-Na and brine waters used for mineral baths and inhalations have a beneficial influence on the skin and act as a disinfectant (Deutsch, Klieber 1982).

Fluoride waters

Eleven waters, mainly from Kłodzka Valley, contain fluorides in concentrations > 2.0 mg dm^{-3} (Jedlina, Cieplice, Lądek, and Busko). The water from Cieplice contains 11-12 mg F^- dm^{-3}, from Lądek-Długopole 7.6-10.0 mg F^- dm^{-3}, and from Busko 3.5 mg F^- dm^{-3}. In Poland, fluorides occur mainly in low mineralized waters: radon waters, siliceous waters and thermal waters (Cieplice), or radon and ferruginous waters (Lądek-Długopole).

The use of fluoride waters in Poland is inadequate. Nowadays, they are used for mineral baths, owing to other properties like the content of sulphur, hydrogen sulphide (Busko, Lądek, Jedlina), radon (Lądek), or as thermal waters (Cieplice). The effect of fluorides on the skin as well as their diffusion have not been fully recognised yet. It is known that fluorine is absorbed by mucous membranes of the mouth and has a positive influence on the structure of teeth (Ogaard 1999). Therefore, such water can be used as mouth wash (also as bottled water, outside a spa) or for manufacturing anti-decay dental products (Czajka et al. 1998, Drobnik 1999, Iracki, Wierzbicka 2005).

Siliceous waters

Waters with silicon concentration higher then 70 mg H_2SiO_3 dm^{-3} are classified as siliceous waters. Five waters from the spas: Cieplice (3 intakes), Świeradów (1 intake), and Kudowa (1 intake) are in this category. The maximum concentration of metasilicic acid of 106 mg dm^{-3} occurs in the intake called Jan II in Świeradów.

With the content of silicon compounds (silicon dioxide, metasilicic acid), the above waters belong to specific therapeutic waters but are not assigned any kind of therapeutic treatment. They are rather an additional factor in the therapeutic properties of mineral baths (Cieplice, Świeradów) or drinking treatment (Kudowa). Siliceous waters contain mainly silicon dioxide in the colloidal state, which participates in mineralization of bones and hardening of connective tissue. Silicon limits permeability of blood vessel walls and keeps the skin and collagen fibers elastic (Puzanowska-Tarasiewicz et al. 2009). For those reasons, siliceous waters are nowadays used more often in cosmetology (Dejneka, Łukasiak 2005, Czerpak, Jabłońska-Trypuć 2008).

Sulphurous waters

Twenty-eight of the analysed waters contain sulphur(II) compounds (H_2S, HS^-, $S_2O_3^{2-}$, HSO_3^-) in a concentration of 1.0 mg dm^{-3} determined idometrically. These compounds occur in concentrations from just a few to hundreds of mg dm^{-3} in 10 spas (Busko, Solec, Wieniec, Horyniec, Swoszowice, Wapienne, Wysowa, Lądek-Długopole, Kudowa, Przerzeczyn). The highest concentration was found in the water (3.97% Cl-Na) from the intake Malina near Solec (830 mg dm^{-3}), in therapeutic waters (1.6-2.0% Cl-SO_4-Na) from Solec (49.6-278.0 mg dm^{-3}) and in Cl-Na waters from Busko (29.7-40.9 mg dm^{-3}). The richest sulphide-hydrogen sulphide resources are in the spas Busko and Solec.

The concentration of sulphides, especially > 20 mg dm^{-3}, indicates that the water is suitable for mineral baths. Sulphurous waters containing <10 mg S(II) dm^{-3}, either low and medium mineralized, are also used as drinking cure. Sulphides diffused through the skin or taken *per os* result in an increased glutathione level in blood serum, -SH groups in tissues, mucosal secretions and histamine release. They also lower the blood sugar level and, by binding heavy metals, detoxify the organism. When in contact with the skin, they produce keratolytic and keratoplastic effects on the metabolism of cutaneous and subcutaneous tissues (Banaszkiewicz et al. 1992). Waters containing sulphide-hydrogen and sulphide are successfully used as a periodontium wash in the periodontitis therapy. These waters, in the raw form, are broadly used in cosmetology, both in spas and at home (added to creams, gels and emulsions).

Radon waters

Underground waters which contain radon in an amount in 1 dm^3 of water that corresponds to the radiation of 74 Bq (2 nCi) are classified as radon waters. Radon occurs in 4 low mineralized acidulous waters in Świeradów (from 96.2 to 592.0 Bq dm^{-3}) and 6 low mineralized waters, fluoride waters, and sulphurous waters in Lądek (from 179 to 1124 Bq dm^{-3}). Radon is found in concentrations from 113.6 to 193.1 Bq dm^{-3} in 0.13-0.22% of acidulous waters HCO_3-Ca-Na in Kudowa and Szczawno. Intakes of therapeutic radon waters, pursuant to the Mining Law classified as basic mineral deposits, occur in the Sudety Mountains and in the Fore-Sudetic Block, which is related to the geologic structure of Lower Silesia (Przylibski et al. 2004).

Radon is a gas with a short half-life time of 3.825 days. It easily evaporates from water during a bath. Therefore, during mineral baths in radon waters, a patient is exposed to radon through the skin and via inhalation. The biological action of radon has not been recognized yet. However, it is claimed that radon stimulates endocrine glands, mainly the pituitary, and stimulates biological processes. However, the latest research shows that radon waters should be used carefully, with each course of treatment adjusted

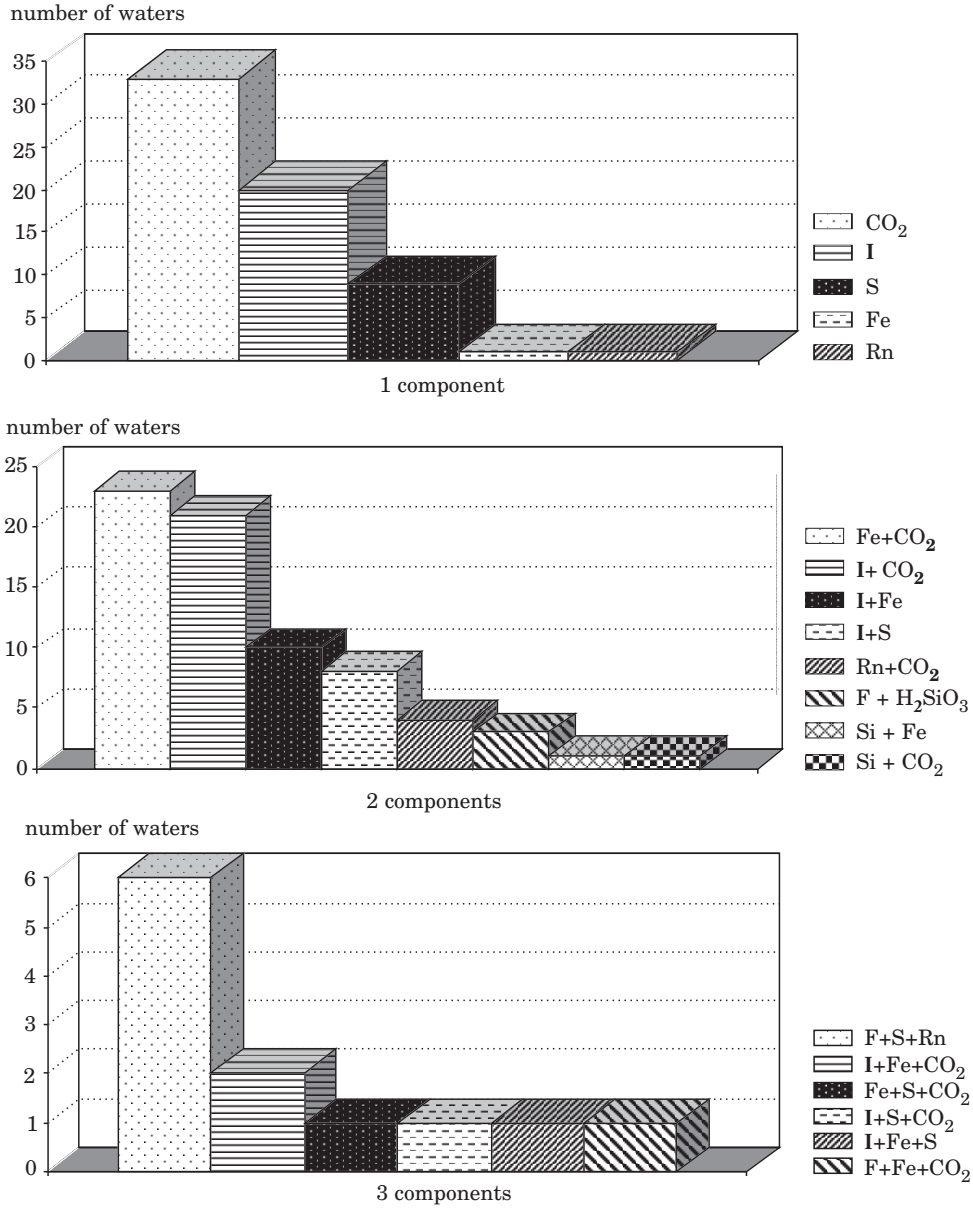

Fig. 1. Type and distribution of specific components in therapeutic waters in Polish health resorts

to an individual patient (FALKENBACH 2000, 2001, FALKENBACH et al. 2000, DEETJEN 1992).

Specific components in significant concentrations suitable for therapeutic purposes occur in different combinations (GUNDERMANN 2009, SCHWARZ, MORSTADT 2010). Sixty-four waters contain one specific component, mainly iodides and carbon dioxide. In 71 waters there are two specific components and 12 contain three types of specific components. The distribution of the specific components is shown in Figure 1.

CONCLUSIONS

1. Mineral and low mineralized specific therapeutic waters from Polish spas are highly varied in the basic chemical composition as well as the type and concentration of specific components.

2. Sulphurous as well as siliceous waters in the raw form are nowadays used in spas most often for the skin care. These waters as well as fluoride waters are used for production of cosmetics (cream, gel, emulsion, paste) used in many spas, beauty parlours or at home for the oral prophylaxis, dental care, hair and skin treatment.

3. Owing to the specific biochemical properties and the number of known groundwater natural resources, sulphurous, iodide and acidulous waters deserve special attention.

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