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Article · January 2011

1 author:

Csaba Varga
University of Pécs
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INTERNATIONAL SCIENTIFIC JOURNAL

March 2012 Vol. 2, No. 1

VOLATILE ORGANICS IN THERMAL SPA WATERS: ACTIVE INGREDIENTS OR ENVIRONMENTAL TOXICANTS?

Csaba Varga[1]

ORGANIC components of medicinal waters should play considerable role in the healing mechanisms ("organic hypothesis"). The author first made an attempt to survey medicinal waters of a country representatively, on their volatile or volatilizable organic composition. Measurements reviewed here are limited to four characteristic types of spa waters in Hungary. The gas chromatograms indicate very different distributions of quantity and quality of organics in spa waters of different hydrogeological origin. The chromatographic fingerprints (together with the exact studies of therapeutic characteristics) may provide scientific bases of a novel classification of medicinal waters. Since Carpathian Basin is a distinct geographic unit this investigation should be extended to its entirety.

Abbreviations: GC: gas chromatography, MS: mass spectrometry, RT: retention time, TDS: total dissolved solid, WWI: 1st world war

1. Introduction

According to the classical approach inorganic compounds of medicinal waters should be therapeutically effective due to their high concentrations. Exact evidences, however, have been lacking for the vast majority of inorganics, so far (Varga 2012). On simply theoretical basis, organic components of these waters should play considerable role in the healing process and balneoprevention (Varga, 2010). If this statement – the "organic hypothesis" – was supported by exact evidences, it could initiate a change of paradigm in balneology, and especially its medical application. Simple gas chromatographic (GC) measurements and the resulting chromatograms – GC fingerprints, together with the exact studies of therapeutic/toxic characteristics – may provide scientific bases of a new classification of medicinal waters. Measurements reviewed here are limited to some typical spa waters selected by hydrogeological origin, in Hungary. Hungary is located in the centre of Carpathian Basin but this latter is a distinct geographic unit therefore these studies should be extended to its whole area, regardless of the recent political (non-geographic) borders. Several spas have been known since the Roman era in the region, involving Pannonia Superior, Pannonia Inferior and, in part, Dacia provinces. For as long as 1000 years, until 1918 one state – the Hungarian Kingdom (Historical Hungary) – involved the whole Carpathian Basin. (The present Hungary is a consequence of a reduction to the one third part of its original territory, after the WWI.) Therefore the most famous, important and popular local spas have already been reviewed – in Hungarian language – from geological, analytical and medical points of view, from the 19th century. Indeed, first analytical data on the inorganic contents of hot springs registered during reign of Queen Maria Theresia were published in the 18th century (Kiss, 2008). While their healing effects were mentioned as early as in 1549. (Balegová, 2008). Carpathian Basin – and especially the central Pannonian Basin, characterized by a thin crust resulting high heat flux – is very rich in hot springs and wells. Other important spas are fed by thermal-karstic sources or Oligocene-Miocene aged aquifers. Nowadays over 1300 thermal wells are recorded just in Hungary. Some of these thermal waters contain high amounts of dissolved organic matter (several tens of mg/L) as indicated by chemical oxygen demand or total organic carbon measurements (Kárpáti et al., 1999). The aim of the present study was to deliver some data to support/reject the "organic hypothesis" by (i) mapping medicinal waters with different origin on volatile organic compounds proposing correlation among organics and health effects, (ii) searching for a simple method to characterize waters for quality assurance of balneological use and finally (iii) supporting the need of reclassification of waters applied in medical balneology.

[1] Csaba Varga, Department of Environmental Health, University of Pécs, Hungary

2. Material and methods

2.1 Description of sampled spa waters

Spas under study are located at the two ends of an EW-axis of Hungary. The exact locations within the Carpathian Basin are indicated in Fig.1.

2.1.1 Hévíz

Hévíz spa (in the vicinity of Lake Balaton) is the largest surface warm water medicinal lake of Europe, showing weak radioactivity, containing Ca- and Mg-bicarbonate and no dissolved oxygen (reductive).

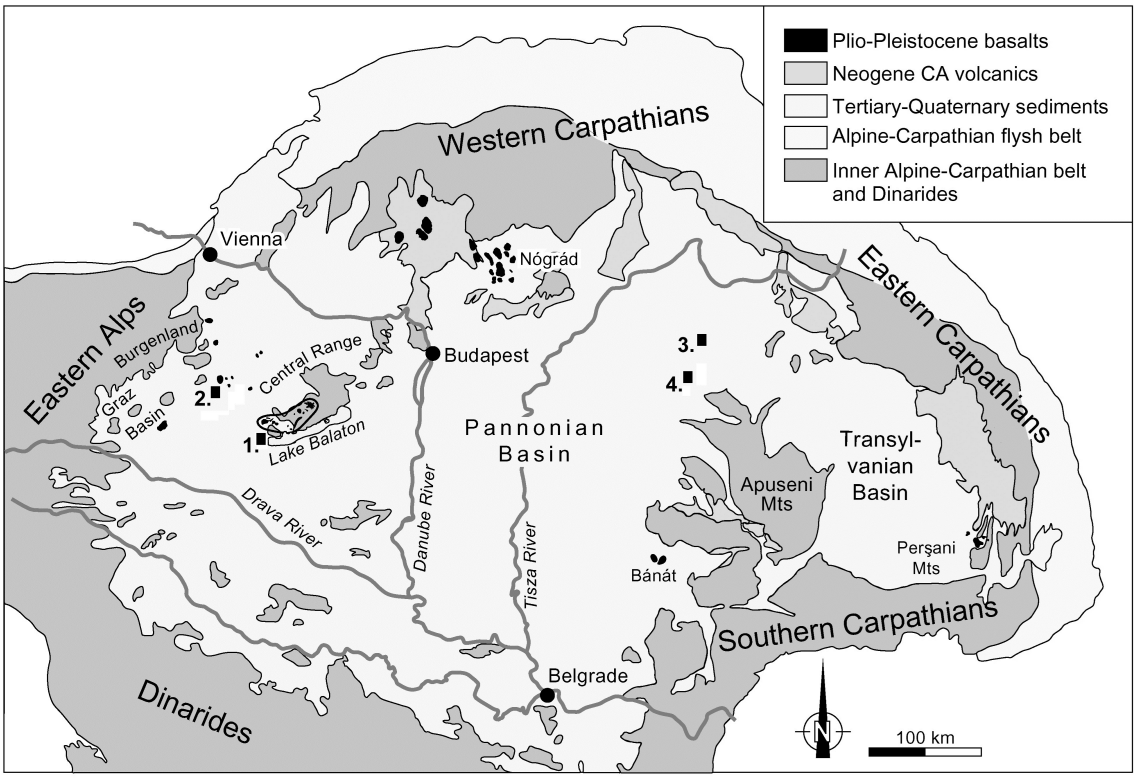

Figure 1. Locations of the studied medicinal spas (■) in the Carpathian Basin (based on the map of the PANCARDI Project, 2010). 1: Hévíz, 2: Sárvár, 3: Hajdúnánás, 4: Hajdúszoboszló. (● indicate capitals of the involved countries)

Colloidal sulphur can also be detected in its water (possibly from carbonyl-sulphide). The 39-42 oC water emerging from a deep spring hall is filtered by inorganic sediment and a peat-bed. The lake is supplied by thermal-karstic type of water, but not rising directly from the Triassic dolomite rather from the Pannonian conglomerate and sandstone. The actual temperature of water at the bathing zone fluctuates seasonally. Hévíz has been the most popular health resort in the rest of Hungary since the WWI.

2.1.2 Sárvár

The 43 oC water is of alkali-bicarbonate and sodium-chloride type with some iodide and bromide. The wells are located in the NW-Transdanubian region tapping a Miocene-aged biogenic limestone layer.

2.1.3 Hajdúszoboszló

The first well was drilled in the 1920's searching for hydrocarbons. The upper-pannonian aquifer yields 73-78 oC hot water rich in minerals: alkali-chloride and bicarbonates, iodide, bromide and fluoride. TDS of the wells varies in the range of 5300-5900 mg/L. This spa water is one of the first recognized medicinal waters in Hungary.

2.1.4 Hajdúnánás

This healing spa is one of the youngest ones. Its sodium-chloride type, iodidated–bromidated mineral water was declared as medicinal water only in 1989. The 1019 m deep well taps Pliocene-upper pannonian layers and produces 67 oC hot water of 7981 mg/L TDS.

2.2 Sample preparation and GC analysis

All samples were taken from the particular untreated spa water and their organic extracts were prepared using a patented procedure involving isolation of organics on macroreticular adsorbent resins (Varga et al., 1998). For the gas chromato-

graphic analysis of the ethanolic eluates (organic isolates) Varian Star 3400 CX capillary chromatograph with the following parameters were used. Column: 30 m x 0.32 mm, quartz capillary; stationary phase: 1 μ m, PTE-5, 5% diphenyl–95% methyl-polysyloxane; septum-equipped programmable injector at 220 oC; temperature programming; flame ionization detector at 280 oC; carrier gas: helium (11 psi, 30 cm/min linear flow rate) (Varga and Groska, 1999). The eluates were analysed immediately, then they were stored at room temperature.

3. Results

GC fingerprints of the studied medicinal waters are shown in Figures 2–6. The first two chromatograms (of Hévíz and Sárvár) are similar but not identical. The fingerprint of Hévíz lake water contains little peaks under the conditions used during the analysis. Only 13 peaks were practically detected in the range of 12-22 min. with a total area of 254,107 counts. (See the chromatogram in Fig. 2.)

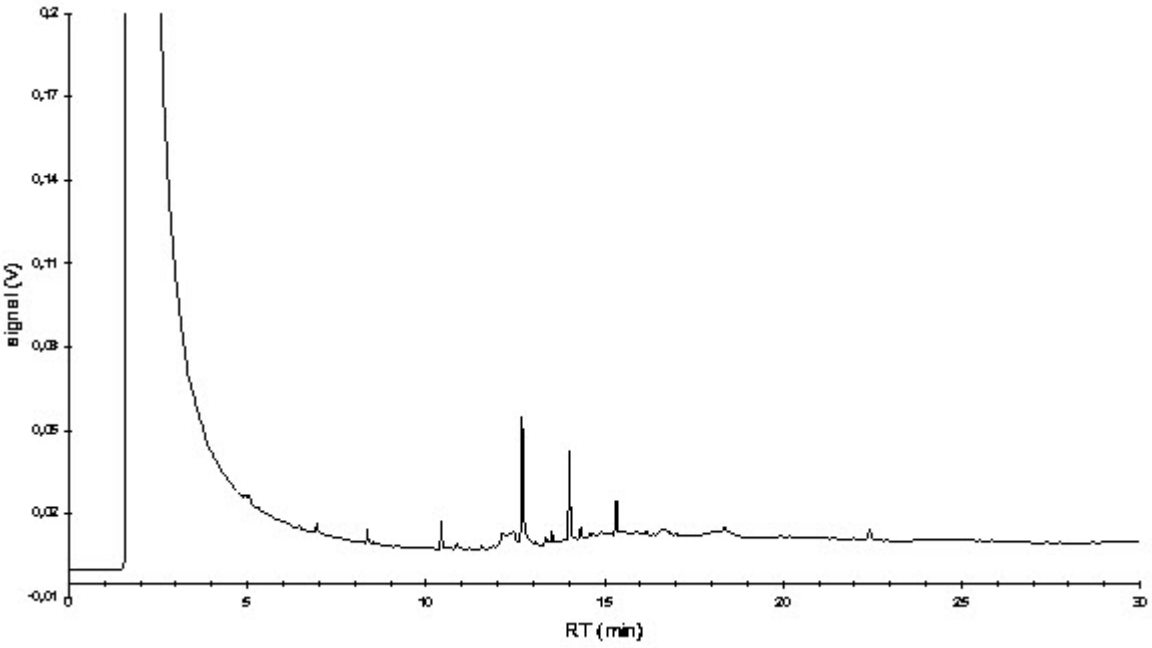

Figure 2. Héviz lake water, gas chromatogram (detector signal in volts vs. retention time)

Highly similar chromatogram can be seen at Sárvár spa water sample (Fig. 3.). The ratio of the detected and rejected peaks were here 26/4 with an area counted 485,864. The highest peaks may be observed in the 10-15 min range of retention time (RT).

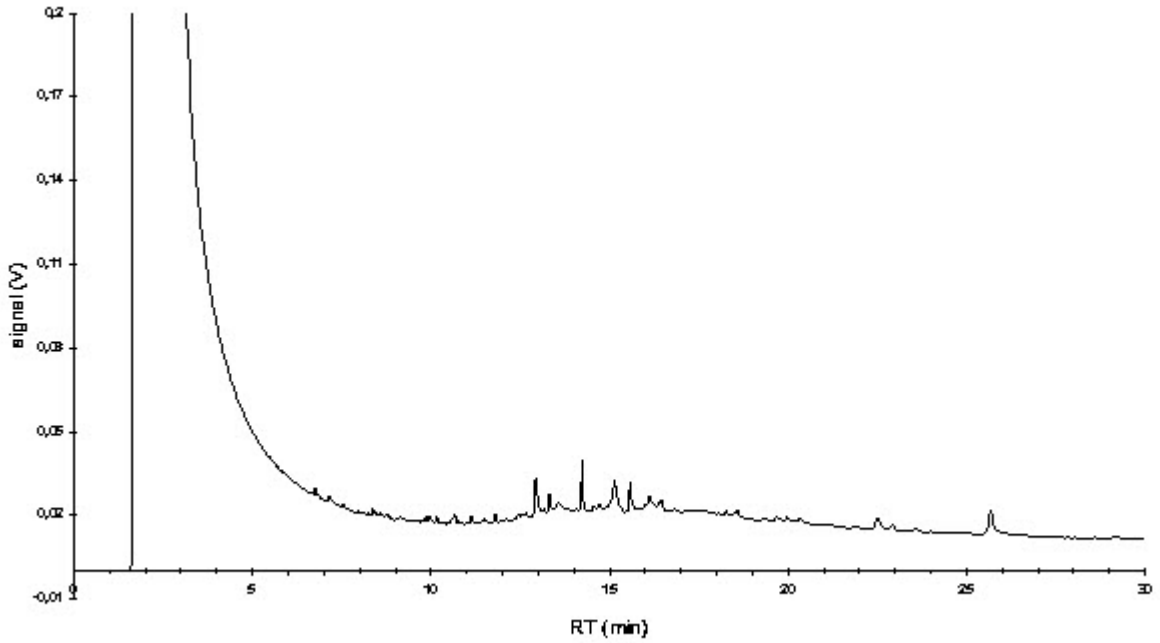

Figure 3. Sárvár spa water, gas chromatogram

Fig. 4. represents a characteristic sample from one of Hajdúszoboszló's hot springs. This sample is practically full of peaks in the RT range under study (128/100 peaks, total area: 10,905,727 counts). Further analyses with Hajdúszoboszló water were focused on the ready-to-use, physically treated (mixed and cooled) spa samples. The stability of the volatile compounds was also checked by comparison of the peaks extracted from the fresh and stored (72-hour) isolates. Meanwhile peak number decreased from 125/98 to 86/61, and total area from 18,121,858 to 4,577,592 counts, some characteristic peaks remained unaltered after the three-day storage at ambient temperature representing some stable and permanent components of the sample.

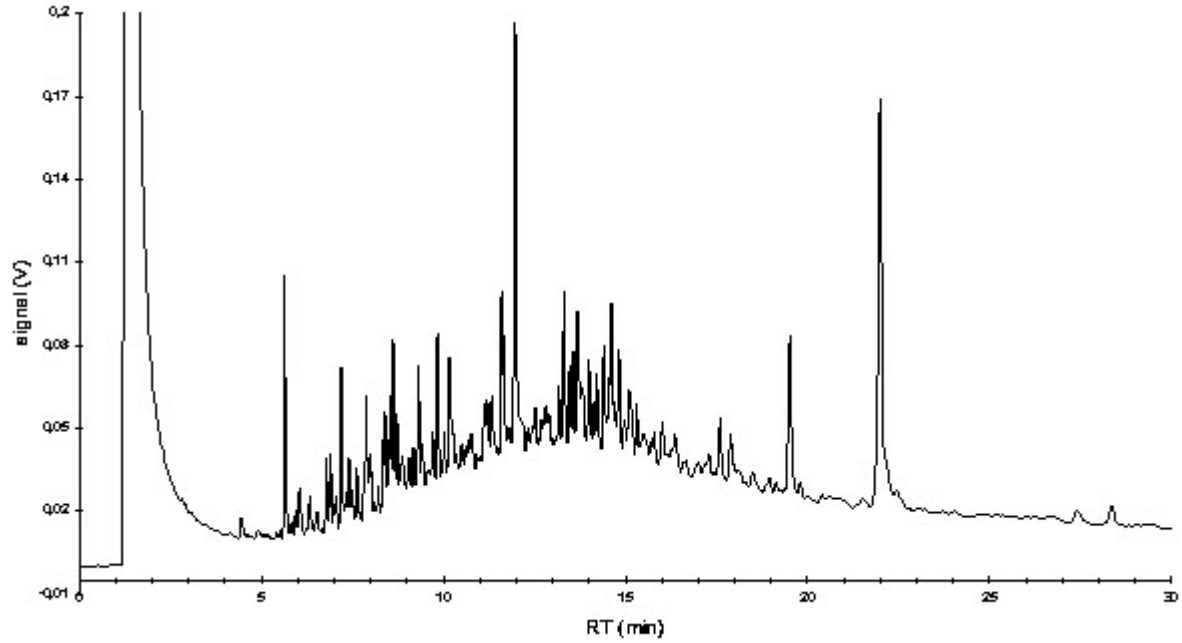

Figure 4. Hajdúszoboszló, "Rákóczi" hot spring water, gas chromatogram

(See Fig. 5a. and b.) The stored isolates did not changed organoleptically. In the final sample (Fig. 6., Hajdúnánás) an unexpected phenomenon was observed. In the originally studied range of RTs the chromatogram is very poor of peaks, but prolongation of the time program supplies relevant information on considerable quantity of lately desorbed characteristic organics. (Accepted peaks: 16, total area: 1,508,564.)

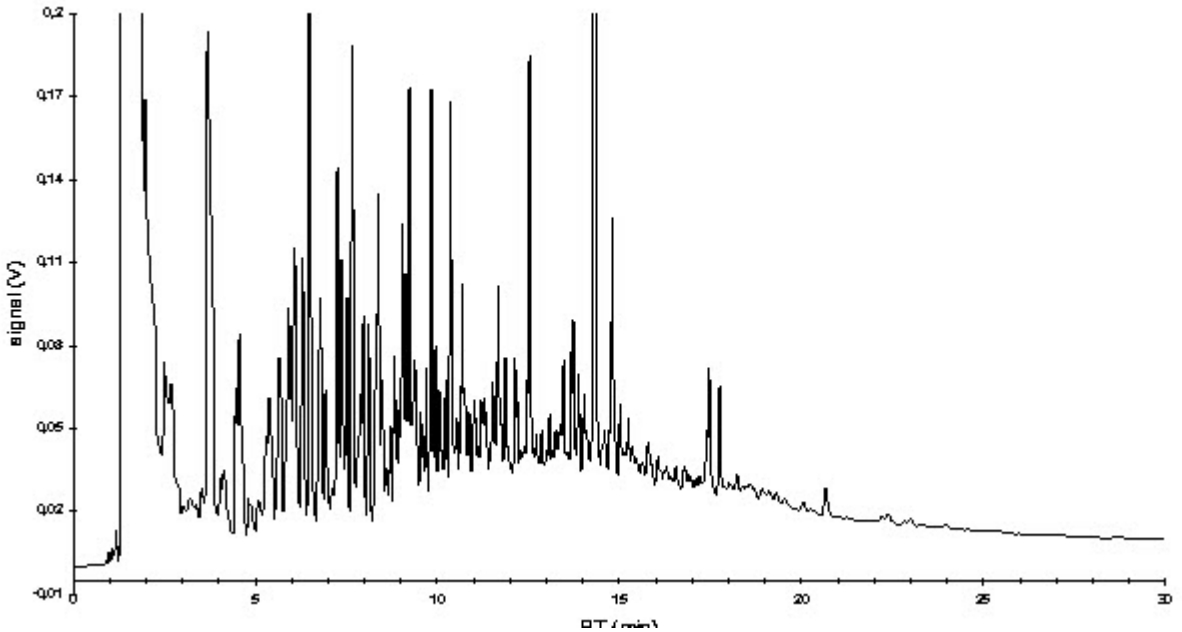

Figure 5a. Hajdúszoboszló mixed, cooled spa water, gas chromatogram of the fresh isolate

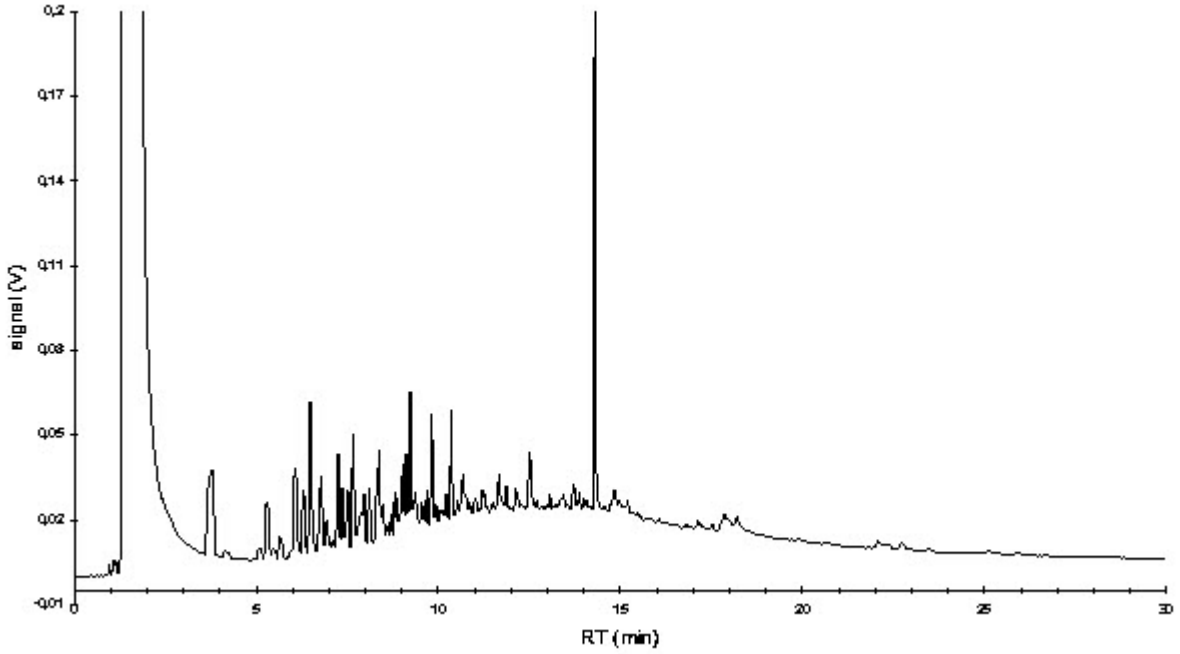

Figure 5b. Hajdúszoboszló mixed, cooled spa water, gas chromatogram of the 72h-sample. As compared to Fig. 5a., characteristic peaks remained e.g. at 3.7; 6.3 or 14.3.

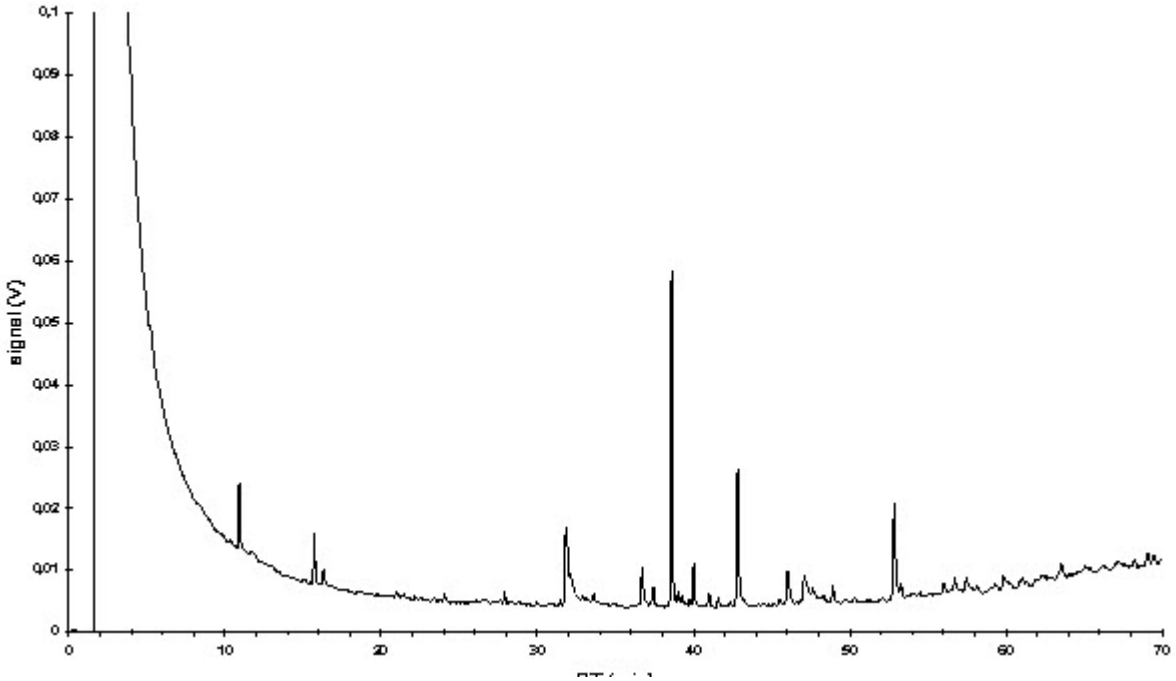

Figure 6. Hajdúnánás spa water, gas chromatogram. The characteristic peaks could be detected only after 30 min.

4. Discussion

So far, spa waters have been characterized by their inorganic composition. The question has arisen whether they could be classified in other way better approaching the therapeutic features. Another issue is the possible association of the organics with the potential toxicity of some spa waters as in case of peloids reported (Szendi et al, 2009, 2012; Gerencsér et al, 2010). Studying the balneological literature very limited information can be found (i) regarding the quantity of organics in medicinal spa waters; (ii) on how constant the distribution and total quantity of organics in a particular spring or well; and (iii) on how different the spa waters are considering quantity and quality of organic substances/fractions. Beside Hungarian springs and wells, some thermal waters of Spain and Italy were only tested from this point of view (DiGioia et al., 2006; Gonzales-Barreiro et al., 2009). Agyagási (1983) published the first study – in Hungarian – on GC and GC/MS analysis of 8 different thermal-medicinal, thermal and potable water specimens. Only mono-unsaturated acyclic olefins (alkenes) were detected by his methods. Geochemists later identified great number of organics in formation waters of the Pannonian Basin, not related to pooled oil. The organic composition of thermal waters also reflects processes leading to their development (Kárpáti et al., 1999; Sajgó et al, 2007; 2007a). Considering the abovementioned facts, furthermore that inorganic-based classification of spa waters does not correspond to therapeutic effects; importance of organic compounds may be much greater than one has thought up to now. The different geological origin and consequently the volatile organic content (representing by the GC fingerprint) may explain differences in the therapeutic characteristics and efficiency. Analysis of fingerprints makes both possible to identify the particular water and follow its changes within a well-defined range. In conclusion, fingerprints can also be used for purposes of quality assurance. It is also true for products made of medicinal waters containing organic concentrates or isolates, since medical products redissolved in hot tap water should show the original fingerprints (Varga et al, 1998, Varga, 2011). The GC fingerprints introduced here suggest that different hydrogeological origin is in close connection with volatile organic content of the particular spa water. Quality and distribution of organics are not related to the inorganic content. Quantities of organics rather reflect to the temperatures of springs or wells. But no doubt, the most problematic issue is the explanation of health effects of spa waters. Several completely different spa waters may effective in therapy of same diseases not depending on their inorganic composition. Of course, we have either no data on the association of organics and therapeutic efficiency yet. How-

ever, biologically active organic compounds, as hormone-like molecules (estrogens), humic substances, oil-, bitumen- or tar-derivatives can have beneficial (or adverse) health effects via different routes of exposure. Experimental neurobiological studies cannot be avoided to clear e.g. the possible psychic action of odour of waters in the healing process; nevertheless, relevant epidemiological studies are also needed focussed on preventive, therapeutic or toxic effects. Volatile compounds evaporate with the water vapour causing the characteristic odour of spas. During the therapy patients inhale several compounds indicated by the fingerprints and this fact may be a considerable factor of healing, together with dermal uptake of volatile and non-volatile organics.

5. Conclusion

These initial steps of mapping organic contents of spa waters of different origin should be followed by deeper analyses and further sampling the whole geographic region. Carpathian Basin is one of the world's richest areas in thermal waters. Therefore it could provide an excellent model region to work out a scientific and evidence-based balneology applying the state-of-art methodologies of analytics, toxicology, experimental medicine and epidemiology. Organic chemical analysis (involving GC fingerprinting) may mean the first step to find the balneological "missing link" between health effects and the chemical composition of waters.

6. Acknowledgement

This work was supported by the Faculty of Medicine, University of Pécs (grant No. 34039). The gas chromatographic measurements were performed by "Liezon Associates", Budapest. Special thanks to Prof. Tamás Bender for critical reviewing the manuscript before submission.

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