

# Mineral Waters of the Slovak Spas – Chemical Analysis, History and Present

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**Abstract:** The basis for understanding the properties of mineral water as a favourable medium for the body is a chemical analysis. While mankind has long gone to the knowledge, thousands of years took place. History of chemical analysis of water began obviously with alchemy, which had prepared some background for scientific analytical chemistry. A criterion for assessing the chemical analyses is the comparability of historical results with the current ones. This criterion may be dated back to the turn of the 18<sup>th</sup> and 19<sup>th</sup> centuries. An example is a comparison of historical and current analyses of mineral waters of the Sliač Spa covering the period 1834 – 2016. Historically, for the documentation of the chemical composition of mineral water in Slovakia the 20<sup>th</sup> Century is the most important. Evaluation and classification of the chemical composition of mineral water is closely linked with exact results of chemical analyses. The first scientific classification of natural waters was developed in 1847 by an American geochemist Clarke. One of the oldest classifications, which are used even today, compiled Palmer in 1911. Slovakia is currently using assessment of natural waters, as proposed by Gazda in 1971 and it's actually a certain modification of the "Palmer system" with greater sensitivity and distinguishing ability of chemical water characteristics. Hereinafter, the paper evaluates mineral water of 18 spas in Slovakia. Distribution of species is made using thermodynamic model and it characterises the proportion of free ions and complexes in water. Interactions water-mineral-gas are ranked based on likely saturation index of plausible mineral phases. From geochemical analysis, it can be said that the dominant mineralization process of formation of mineral waters of the spa is the dissolution of carbonates. The second process that can significantly affect the resulting chemical composition is the dissolution of gypsum. Silicon is present in the mineral waters in particular in the form of un-dissociated  $H_4SiO_4$ . Acceleration of virtually all geochemical processes is alleviated by high levels of carbon dioxide, water temperature in the collector and a long residence time of groundwater in the rock environment. The result is a high TDS value in the range of 1,299 – 29,903 mg · l<sup>-1</sup> (except for acratotherms). In addition to water-rock-gas interaction in some mineral waters of spas an important role play biological processes (presence of  $H_2S$ ) and preserving relict marine water.

**Key words:** alchemy, analytical chemistry, balneology, classification of mineral water, thermodynamic model, distribution of species, mineralization processes

## 3.1 Introduction

Mineral water differentiates from ordinary groundwater by its chemical composition and physical properties. It can be stated that it represents a natural anomaly that

has developed due to specific geological, hydrogeological, geochemical and tectonic conditions and is stored in the hydrogeological structure.

The mineral waters from the viewpoint of chemical composition contain the same substances as the ordinary groundwater, but in larger amounts, and in other quantitative ratios. Simply speaking, the solutes form three groups. The first group are compounds which are present in large quantities. Among the cations  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  are present and among the anions  $HCO_3^-$ ,  $SO_4^{2-}$ ,  $Cl^-$ . The second group represent on the order less abundant cations such as  $Li^+$ ,  $NH_4^+$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$  etc., among the anions  $Br^-$ ,  $I^-$ ,  $F^-$ ,  $NO_3^-$ ,  $AsO_4^{3-}$  etc., among the non-electrolytes  $H_2SiO_3$  and  $HBO_2$ . The third group represent trace elements  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$  and others. Similar conditions are valid for dissolved and free gases. High content may have gases  $CO_2$ ,  $CH_4$  and  $N_2$ . On order lower is the  $H_2S$  content. Some of the mineral waters are enriched with radium and radon, others contain smaller quantities of helium and argon. The groundwater turns to the mineral water by exceedance of a certain limit in the content of dissolved substances and gases. To determine the quality of mineral water and its use in balneology it is necessary to quantitatively determine various cations, anions, gas content and its physical properties.

The paper presents the development of knowledge about mineral waters through their properties and composition. It resides in historical documents and current chemical composition of water in 18 spas in Slovakia with recognized natural healing waters.

## 3.2 History of chemical analysis

Using of natural mineral water for therapeutic purposes dates back far into the beginning of human culture. First it was interest in learning about water and its force as impact on natural processes, but also on the human body. As early as 604 A.D., Lao Tzu, Chinese philosopher and founder of Taoism quoted: "Water is the softest thing, yet it can penetrate mountains and earth". An admirable knowledge at that time, which recognized in nature the action of two materials without the knowledge of geochemical processes. The beneficial effects of water on the human body apparently had roots in the principle of "try and see", for example, effects of thermal water, etc.

The knowledge of the water composition was examined in the past mostly by alchemists. The alchemy was the art, how to separate a part of the universe from existence in time and achieve improvement of this part, which meant gold for metals, longevity for man and his immortality. Improvement of the material was sought by action of various media (philosopher's stone for metals, the elixir of life for the people), while spiritual enlightenment evolved smoothly from an uncovered form.

The alchemy extends its beginnings in ancient times, it runs through the entire Middle Ages and its traces are still observed in the first century of Early Modern Times. Epicentre of the alchemy was probably in China, from where it spread to India, ancient Egypt, and from there to Greece. In Europe, alchemists focused more on metals. For centuries, there was a belief that there are only seven metals, i.e. the same number as then known planets. The pinnacle of European alchemy is considered the period of rule of Emperor Rudolf II; in his courtyard many alchemists like Kelley, De Brahe, Kepler and others, were active.

In the 17<sup>th</sup> Century iatrochemistry had unfolded that the production of gold, the philosopher's stone and the elixir of life was replaced by the care of people's health and chemotherapy. Its main representative was Paracelsus, who began to use inorganic materials in the treatment, especially those of antimony and mercury. Paracelsus is also considered the founder of toxicology mainly because he defined the poisons in the form of "any substance is a poison, it depends only on its quantity".

From this brief characteristics of alchemy is clear that, in fact, it had not been science, but philosophy. On the other hand, it should be noted that the period of alchemy was beneficial for modern chemistry for example, it brought distillation apparatuses, mortar, banks, the development of basic experimental procedures and techniques, and not least the discovery of full range of elements and compounds.

From chemical discoveries it should be mentioned that after the 11<sup>th</sup> Century sulphuric acid was known, termed the spiritus vitrioli or oleum vitrioli. The term vitriol for its glassy appearance (from the Latin vitreus – glass) was used to term crystalohydrates of metal sulphates, of which it was produced. Inter alia, it was also acquired by the decomposition – "distillation" of alums. Hydrochloric acid was obtained by the action of sulphuric acid on common salt. It was called spiritus saline. To this day it is called in German Salzgeist, that is the spirit of salt. Similarly, it was known as nitric acid mixture produced by saltpeter (sodium nitrate or potassium) heating with a mixture of copper sulphate and alums. There exist a description of aqua regia from 1270, which was prepared by the action of nitric acid upon ammonium chloride. In terms of the development of chemistry, after the discovery of iron the discovery of strong mineral acids was the biggest achievement. The time difference of the two discoveries is 3,000 years. Random discovered reactions of acid with potash (potassium carbonate) and other bases such as calcium hydroxide, and carbonates, gave impetus for the systematic examination of reactions for the preparation of salts, which we would

term now neutralization reaction. Among other inorganic reactions there were disclosed reactions for the preparation of silver nitrate by dissolving silver in nitric acid and the preparation of silver chloride by hydrochloric acid action on nitrate. Copper was prepared by the so-called cementation, which is the effect of non-noble metal, for example, iron on solutions containing soluble copper compounds. Red mercuric sulphide was prepared synthetically, i.e. the mineral cinnabar, namely by direct compounding mercury and sulphur, which was very helpful in understanding the chemistry of mercury. Cinnabar was known already in ancient times as a medicine. Our predecessors already recognized a number of other mercury compounds. They did prepare various forms of iron oxide, in particular as colorants. By stibnite heating (antimony sulphide) with iron pure antimony was prepared and recognized as a new metal.

After completing 30 Years' War (1618 – 1648) and its hardships the alchemy faded away. This period can be called transition with regard chemistry as a science. Great advances of the 18<sup>th</sup> Century were achieved by the fact, that the issues discussed were focused on the problem of combustion, resulting in the so-called phlogiston theory. This theory was introduced by G. E. Stahl, who had used in support few ideas of his teacher J. J. Becher. Late 18<sup>th</sup> Century A. L. Lavoisier disproved all the arguments of the phlogiston theory and replaced them with new theory of oxidation.

The 19<sup>th</sup> Century was in the field of analytical chemistry a period of consolidation. New scientists emerged with their discoveries, as Lomonosov, Lavoisier, Dalton, Avogadro, Mendeleev, Nobel and many others. From a methodological point of view there were used gravimetric and volumetric methods of analysis. Instrumental methods became important for analytical chemistry by the end of the 19<sup>th</sup> Century. Almost immediately after its discovery a spectroscope was accepted as a means of qualitative analysis. Important role gained a refractometer and a polarimeter not only in purely scientific laboratories, but also in practice in the Food and Drug Administration.

### 3.3 Chemical analysis of water

Chemical analysis of water enables a detailed view of its composition, properties, applications and ultimately provides a picture of its origin. Very nicely this view can quote convey of important Slovak poet A. Sládkovič: "Alas, who sees in the sea only water, who can't hear a deaf nature, who sees in the stones just stones".

The healing effects of various mineral waters in Europe are described in books and articles about the year 1500. To complement the medical information on the effects of mineral water, some authors attempted to explain the chemical composition of dissolved salts. For example, a Spanish physicist Limon Montero 1697 divided water into two groups – drinking water and mineral water. Drinking water containing negligible amounts of solutes, and mineral waters containing minerals and metals in a significant content. These solid materials enrich the water by circulating through the rock and minerals. Like almost authors before

about 1770, Limon Montero did not have neither a clear concept of the chemical composition nor relative amounts of material in the water (Davis & Davis, 1997).

Scientific basis of balneology has been systematically built up since the 18<sup>th</sup> Century, when there were recorded the first chemical explorations of mineral waters. In the first issue of the scientific journal “Physical and Chemical Essays” (1779), Torben Bergman, Professor of Chemistry and Pharmacy at Uppsala University in Sweden, wrote about chemical analysis of natural waters, including the mineral ones. He noted that if the weighed amount of mineral water is evaporated in the smoke, the weight of the residue is negligible compared to the weight of water; however, the residue may comprise six to eight earth metal salts and ingredients. Bergman said that “accurate water analysis can be considered as one of the most difficult problems in the chemistry” (Bergman, 1779). Although there were problems of identifying small quantities of salts with similar chemical properties, there was no guarantee that the residue will contain the same compounds as mineral water. This means that at the analysis of mineral water, the chemists have encountered many difficulties. The analyst had to be smart and to have a lot of experimental experience. Most of those who wrote on this topic in the Seventeenth to the early Nineteenth centuries were physicians practicing medicine in spas. Among the most famous belonged Robert Boyle and Friedrich Hoffmann. The work by Boyle “Memoirs of a natural history of mineral waters”, published in 1685, contained many original solutions with regard to the knowledge of the time. The introduction stated that it was necessary to take into account geological environment, through which a mineral water passes. Then followed the tests – temperature and density of water (using a hydrostatic scales), transparency, colour, smell. To put water drop under the microscope and examine how many moving particles appear in it. To detect and observe sediment and particles formation during storage on the air, during the boiling and freezing process of water. To measure viscosity. After these tests, subsequent chemical examination of water and distillation residue follow. Boyle also used tannin solution to test the presence of iron (black colour) and copper (red precipitate). He stated that the tannin should be carefully added, because the intensity of colour indicates the number of elements in the water. He proposed also other agents – rose extract, pomegranate extract, Brazilian wood, etc. He described the new reagent, which he called “volatile sulphurous spirit” that gave with the lead a black colouration. Boyle studied many reagents to prove the chemical elements. Several authors agree that he was the actual founder of chemistry as a science. Boyle separated chemistry from medicine, and gave it a new direction.

Another important book is by Hoffmann “Methodus examinandi aquas salubres” which was published in 1703 (Coley, 1990). In this book he described the analyses of many types of mineral waters. His work was underpinned by the knowledge described by Boyle. The components that were recognizable in the mineral water were sodium, potassium sulphide; iron was indicated by the presence

of red colour in the sediment. The presence of dissolved iron he indicated by the presence of carbon dioxide. If carbon dioxide was expelled by boiling, iron fell out of solution. In the same way, he showed the presence of Fe, which came out of solution as vitriol (iron sulphide). The presence of alkali metals he determined with ammonia. He also discovered the presence of magnesium salts and separated them from calcium salts. Sulphidic waters he determined with silver salt by formation of black silver sulphide precipitate. Hoffmann had the belief that water is a complex of etheric and solid substances. Hoffmann’s work is recognized as a significant contribution to the chemical examination of mineral water, but described chemical tests which he introduced, cannot be classified as a systematic method for the analysis of mineral water. This became an important goal of later authors of the Eighteenth Century (Szabadváry, 1966).

The first one who attempted to systematize the analysis of mineral waters in England was Thomas Short, doctor from Sheffield, who wrote about some English mineral waters in 1730 (Coley, 1990). Short criticized all previous analysts of mineral waters, including Boyle and Hoffmann and tried, though without much success, to develop methods of mineral waters testing, using proven agents such as vegetable colours, silver nitrate, mercury salts, sugar, certain acids, ammonia. While he was able to identify some of the basic compounds of mineral waters, he didn’t manage to determine volatile components, which had healing properties.

In 1740 William Brownringg, doctor of Whitehaven, conducted experiments with water from spas in Belgium. He came with the recognition that volatile gases from the mineral waters were the same as gas from coal mines. The publication was issued in 1765 (Hamlin, 1990). Later in 1770, Bergman recognized the importance of dissolved air in water; he named it as a “direct acid”. He identified the hydrogen sulphide and nitrogen in various mineral waters. To determine the sulphates he used barium chloride, to evidence chloride, he used silver nitrate, concentrated nitric acid for evidence of sulphides, oxalic acid for the detection of calcium, ferrocyanide for iron. Bergman knowledge of the composition and the analysis of mineral waters created scientific basis in the coming years.

One of the drawbacks of investigators of that time was the fact that they expressed the components of mineral waters as solid salts. For example, the ions  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  they expressed as  $\text{CaSO}_4$ . Only in 1900 upon Arrhenius (1859 – 1927) discovery of the theory of dissociation and ionization, the scientists began to take into account the elements in ionic form. Analyses of mineral water were “almost” complete, expressed as the elements in ionic form (Palmer, 1911). In Tab. 3.1 the chemical elements are included with the date of their discovery in waters (Hammond, 1967).

Major innovation of mineral water analyses was the discovery of spectrographic method by Robert Bunsen and Gustav Kirchhoff. In 1857 Bunsen devised a method to identify volatile metals in the flame using a platinum wire. The proof resided in different colours of the flame for each element. Three years later, in cooperation with Kirchhoff,

Tab. 3.1 Date of discovery of some chemical elements, important for water analysis

Element	Discovery date	Scientist credited with the discovery
Boron	1808	Davy, Guy-Lussac, and Thenard
Bromine	1826	Balard
Calcium	1808	Davy, Berzelius, and Pontin
Carbon	Prehistory	-
Chlorine	1810	Davy
Fluorine	1886	Moisson
Iodine	1811	Courtois
Iron	Prehistory	-
Magnesium	1808	Davy
Nitrogen	1772	Rutherford
Oxygen	1775	Lavoisier
Potassium	1807	Davy
Silicon	1824	Berzelius
Sodium	1807	Davy
Sulphur	Prehistory	-

he contributed by important improvement of the method. Coloured light from the flame they left to pass through a prism and to reflect a spectrum at a white wall. Almost immediately they discovered two new elements, caesium and rubidium. Only a very small amount of sample was needed for the detection of elements by spectroscopy. Since 1860, thanks to their sensitivity and comfort the spectroscopic methods belonged among the most important methods for the analysis of groundwater.

Given the nature of related problems, it is easy to see why those who tried to reveal the chemical composition of mineral water in the Eighteenth Century met with many difficulties. Even the simple technique – evaporation of water, which enables to obtain the dissolved solids in the solid form, was a problem for a chemist of that time (Coley, 1990).

Currently, the analysis of mineral waters still means a challenge at solving complex matrix, although the development of methodologies in the Twentieth Century progressed enormously. For the analysis of mineral waters techniques are now routinely used such as gravimetric, volumetric analysis, electrochemical methods, spectrophotometry, ion chromatography, atomic absorption spectrophotometry – flame, hydride generation, electrothermal atomisation, atomic emission spectrometry with inductively coupled plasma and the latest techniques for the determination of elements in ultra-trace concentrations – mass spectrometry with inductively coupled plasma.

### 3.4 Chemical analyses of mineral water in Slovakia

Obviously, in the amount of historical information on the chemical composition of mineral water in Slovakia, it is impossible to designate any analysis by the term “the

oldest chemical analysis of mineral water”. This is due to a variety of criteria on this issue. If we choose a criterion – the comparability of historical analyses with the current ones, it can be said that revolution in analytical methods and the expression of the results of chemical analysis occurred at the turn of the 18<sup>th</sup> and 19<sup>th</sup> centuries. In the chemical analyses of the early 19<sup>th</sup> Century, there were already the breakdowns of the contents of the main components expressed in the form of salts. Later, this form of expression changed using the oxides, e.g. CaO, MgO, R<sub>2</sub>O<sub>3</sub>, etc. The current form of expression of the results of chemical analyses in ionic form was launched at the beginning of the 20<sup>th</sup> century.

History of learning and discovery of mineral waters in Slovakia is very well described in translations and works of A. Rebro (Rebro, 1983, 1996 and others). Definitely, the father of balneography can be regarded J. Wernher who by his work “De admirandis Hungariae aquis hypomnemation”, published in 1556 in Basel, stunned the then world. He systematically described and represented 22 sites of mineral water. He was interested in and examined the properties of waters. In Špania Dolina Valley, where copper was mined, there were reports about the source from which greenish water flows out, in which can be found after settling grains of chrysocolla. At Sliáč he described a depression with malignant vapours. When above this depression the stick tied cock or hen were tentatively shoved, leaving them under the influence of vapours, these birds so quickly perished, as though they were strangled (Wernher, 1556). It was probably the depression with expelled carbon dioxide, that at that time people were not yet aware. From a chemical point of view, the most famous is description of copper acquisition from mine waters in Smolník. Practically it was a process (popularly cementation), where less noble metal (using the pieces of pig iron) precipitated copper from water.

Interesting contribution on the composition of mineral water provided Tomas Jordan from Cluj by work “O vodách hojitedlných neb teplicech moravských” (*On healing and thermal waters of Moravia*) in 1581. He described them in Trenčianske Teplice. The work also provided information about collection of undisturbed sample of water, which was carried out in such a manner, that he charged the servants to emplace to the bottom of the pool a pitcher closed with a cork stopper. This was opened by one servant who took the water in the pitcher, closed it and the second servant pulled him by his legs above the water. The pure sample was subjected to distillation. What remained after distillation resembled the pharmacists copper sulphate, which is also called alumen plumeum. If it was put on the fire, whiteness was not lost. Therefore he concluded that hot water of Trenčín contained a lot of very fine sulphur fumes and with them was also a large amount of mixed sulphate (alum).

Significant work was compiled during the Habsburg Empire by Johan Heinrich von Crantz in 1777. The work was created as a summary of the results of the first official registration of mineral resources from the years 1763 – 1769. It was a huge work with 306 pages con-

taining a sources register. From Slovakia he described 158 sites with mineral water, which in many cases appeared in writing for the first time. In terms of chemical analysis, the work is very inconsistent (supplied by many informants) and consists of some experiments with a variety of acids, salts, and dyes to characterize the chemical composition of water. An example of one page of the original of this work, which describes site Gánovce, is on Fig. 3.1.

First older chemical analyses, which could be already compared with the current ones were made in the early 19<sup>th</sup> Century. In these cases, at the analyses adjustment, there may occur various irregularities, which were summarized by Hyánková (1989):

- Inconsistencies in the marking and naming of mineral water sources and sites of their occurrence;
- Inconsistencies in the use of chemical terminology, in which there were used various combinations of German, Hungarian and Latin names of individual compounds;
- Inconsistencies in the form of expressing bound carbon dioxide, mostly referred to as carbonates;
- Incompleteness of chemical analyses in terms of representation of the main ions;
- Inconsistencies in the quantification of results, which were in the old analyses somewhere expressed in grans for 16 ounces, or 32 ounces, and sometimes also in the pharmaceutical, or civilian pounds.

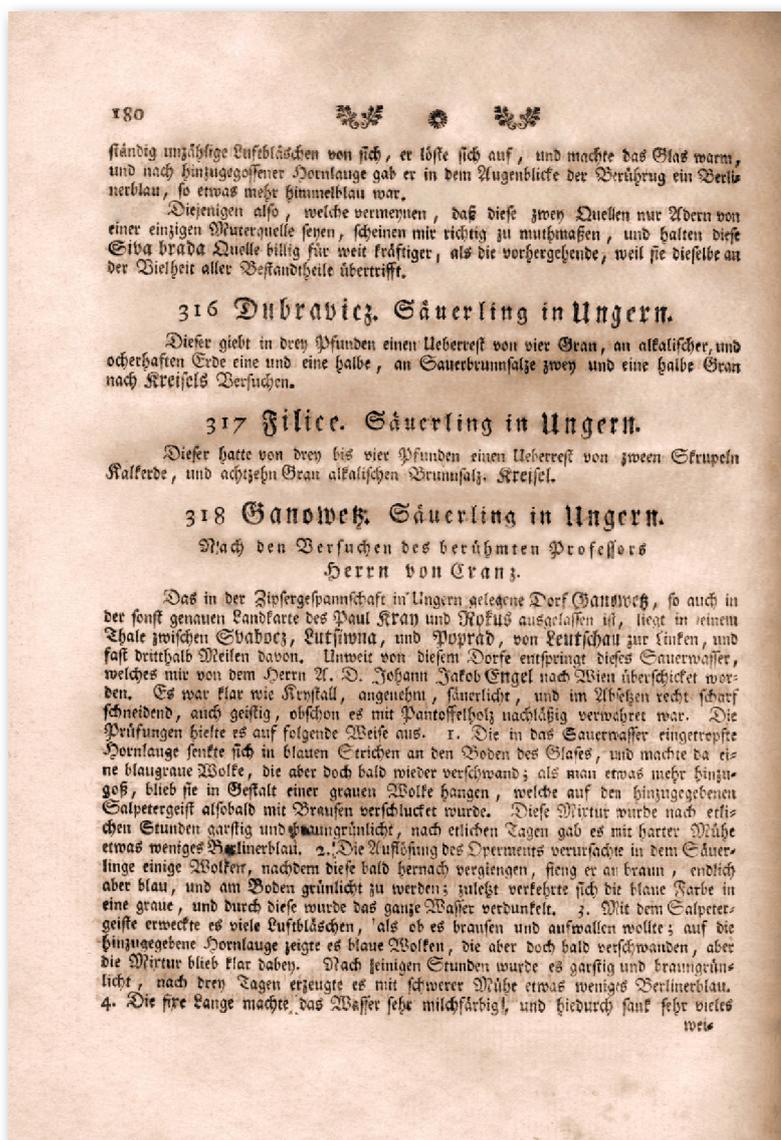


Fig. 3.1 Example of the work by von Crantz (1777) – Gánovce

Tab. 3.2 Chemical analyses of the source Sliáč Kúpeľný from various periods

Year of analysis	1834	1855	1882	1921	1950	1967	2016
Analyst	Wagner	Hauch	Than	Prokeš	Nemejc	*	**
Na	sum (Na+K)	sum (Na+K)	56.4	65.36	57.9	57	58.49
K	134.9	104.4	36.9	43.25	32.3	34.2	39.36
Li	2.08	3.87	0.05	0.05	1.1	1.37	0.228
Ca	621.8	643	639.9	643.82	699.2	709.42	685.78
Mg	126.7	217.9	184.8	151.84	188.1	184.83	174.36
Fe	2.7	9.58	7.57	9.51	1.83	7.2	2.44
Mn	-	-	0.65	0.72	-	0.8	1.01
Cl	7.2	4	4.42	6.12	4.3	51.93	6.38
SO <sub>4</sub>	1,375	1,632	1,534	1,750.55	1,540.4	1,630.77	1,584.7
HCO <sub>3</sub>	880.7	1,304	1,158	763.65	1,316	1,195.6	1,162.4
H <sub>2</sub> SiO <sub>3</sub>	37.7	15.6	30.7	35.3	-	13.19	15.84
CO <sub>2</sub>	1,200	1,301	1,269	1,468.8	-	1,415	1,749.88

Note: results in mg · l<sup>-1</sup>, \* Franko et al., 1975, \*\*ISS MoH SR

As an example of a comparison of chemical analyses Location Sliach is presented. The recalculated analyses since 1834 to the most recent from 2016 were at disposal (Tab. 3.2). The analyses of the years 1834 and 1855 are incomplete because they express sodium and potassium content as summation and they lack determination of manganese. In other analyses, the contents of Na and K are comparable, indicating both the analytical precision and the stability of the two components. Lithium content varies in the range of  $0.05 - 3.87 \text{ mg} \cdot \text{l}^{-1}$ , which can probably be explained by an analytical technique other than that of the last test (Analytical Method ICP-AES). The content of calcium and magnesium is likely to be comparable, and is highly dependent on the chemical stabilization of the samples taken to the laboratory. It is still possible certain dispersion of values that can be caused by different contents of carbon dioxide over time and depending on the sampling of mineral water. The content of bicarbonate can be assessed similarly.

From the viewpoint of historical documentation of the chemical composition of mineral water in Slovakia the most important is 20<sup>th</sup> Century. The first one was “Balneography of Slovakia” (Hensel, 1951). The author illustrates the chemical analyses of the 46 spas in Slovakia. In addition, the work also analyses indicated non-spa sources classified according to the then districts. The work also contains analyses of gases and peloids. Another important work is the “Mineral waters of Slovakia, balneography and crenography” (Krahulec et al., 1977, 1978). As the name suggests, it consists of two parts, the first is balneography in which the chemical analyses of 17 spas are presented. The second part consists of practical results of registration of mineral water in Slovakia by districts. In the then registration there were recorded around 1,200 mineral water sources. Very important is the third work “Genesis and classification of mineral waters of the Western Carpathians” (Franko et al., 1975). The work includes 81 chemical analyses of mineral waters. Significant, however, is the hydrogeological and hydrogeochemical assessment. The work provides essential information for understanding the formation and genesis of mineral waters in Slovakia.

### 3.5 Classification of the chemical composition of mineral water

Classification of the chemical composition of natural waters is practically linked to the very beginning of the examination of the content of total dissolved solids and gaseous substances in water. In connection with the increased use of mineral water for spa and therapeutic purposes and advances in analytical methods there have been accumulated a considerable number of chemical analyses mainly in Germany and Russia. At that time, typing of mineral waters according to chemical composition did La Rue in 1779 and Hofmann in 1815.

The first scientific classification of natural waters drew up in 1847 the famous American geochemist F. Clarke. He divided the waters according to three basic characteristics:

- Dissolved salt content;
- Hardness (summation of salts of alkaline earth elements);

– Alkalinity (summation of salts of constant acids); whereas the results of chemical analyses he expressed in the form of oxides and anhydrites.

Rather large milestone in the expressing of the chemical composition of waters was drawn up by Viennese chemist C. Than in 1864, who proposed an equivalent form. This was later elaborated with S. Arrhenius, W. Ostwald and others. These authors showed that in aqueous solution the individual components are not in the form of oxides and salts, as was previously believed, but in the form of cations and anions.

Another important factor that influenced the reporting of results of chemical analyses was elaboration of definition of a system of combining acid (or anions) and bases (or cations). In the mid-19<sup>th</sup> Century Bunsen (1874) and Fresenius (1876) submitted two different ways of such a combination. The Bunsen method consisted of a sequence of loss of salt from a solution at water evaporation. The Fresenius method consisted in the gradual emergence of chemical compounds in relation to their reactive acids and bases in a row  $\text{Na}^+/\text{K}^+/\text{Mg}^{2+}/\text{Ca}^{2+}$ ,  $\text{NO}_3^- - \text{SO}_4^{2-} - \text{HCO}_3^-/\text{CO}_3^{2+}$ . It can be said that the principles of Fresenius – combination of cations and anions in the direction of decrease in the solubility of the salts, wherein the content of cations and anions is represented by C. Than in equivalent values, have become virtually permanent scientific basis for the development of hydrochemical classification of natural waters. One of the earliest classifications of this type is the classification of C. Palmer, published in the USA designed by Stabler (1911) and amended by Rogers (1917). It is based on so-called “Palmer Indices”.

The classification of medicinal mineral waters, according to Hynie (1963) sets out two basic directions – medical and chemical, or chemical – geological. The medical direction classifies water according to representation of ions in solution in relation to the human organism and the chemical – geological one actually to determine the genesis of mineral water. Hynie (1963) draws attention to one of the most important things: “We cannot alter or combine balneological classification systems and nomenclature with geochemical classification systems and nomenclature, applicable to all natural water”.

Jetel (1975) essentially divides the classifications of the chemical composition of natural waters into genetic and descriptive ones. At the genetic classification the abovementioned author provides an interesting remark: “Classification which, based on formal chemical or physical parameters, would allow for unambiguous genetic classification, does not yet exist, and it is uncertain whether it can exist”.

Geochemical issues of mineral waters in the Western Carpathians, based on data by Hensel (1951), were dealt with Mahel’ (1952), later by Hynie (1963). The formation and classification of mineral waters of the Western Carpathians is in the focus of the work Franko et al. (1975). In this work, for the division of the mineral waters according to the chemical composition, the classification by Gazda (1971) is used. This is a modification of Palmer’s classification system, where in addition of the principle of ion

combinations the principle of the prevailing characteristic is used. This classification eliminates small resolution of the original Palmer’s indices by splitting the first and second salinity on the chloride, sulphate ones and nitrate, as appropriate. The other division of the second salinity into magnesium-chloride and calcium-chloride components allows to build on other classifications, such as by Alekin, Sulin, etc. It further distinguishes on the principle of the prevailing characteristics basic, intermediate and mixed types of water. The above classification is still used in Slovakia to evaluate groundwater, in particular, and mineral and geothermal water in its scope.

### 3.6 Characteristics of the components of mineral water of spas

Geochemical characterization of mineral water of spas is made on the basis of assessment of 18 spas in Slovakia. Because in individual spas there can be mineral water sources of different chemical composition, their choice was made so that the spas having several such sources are represented by several analyses in the selection. Chemical analyses represent the situation of 2016. Some discrepancy in the number of spas is due to the fact that in the Čižstov site the spa is currently not operated (Fig. 3.2).

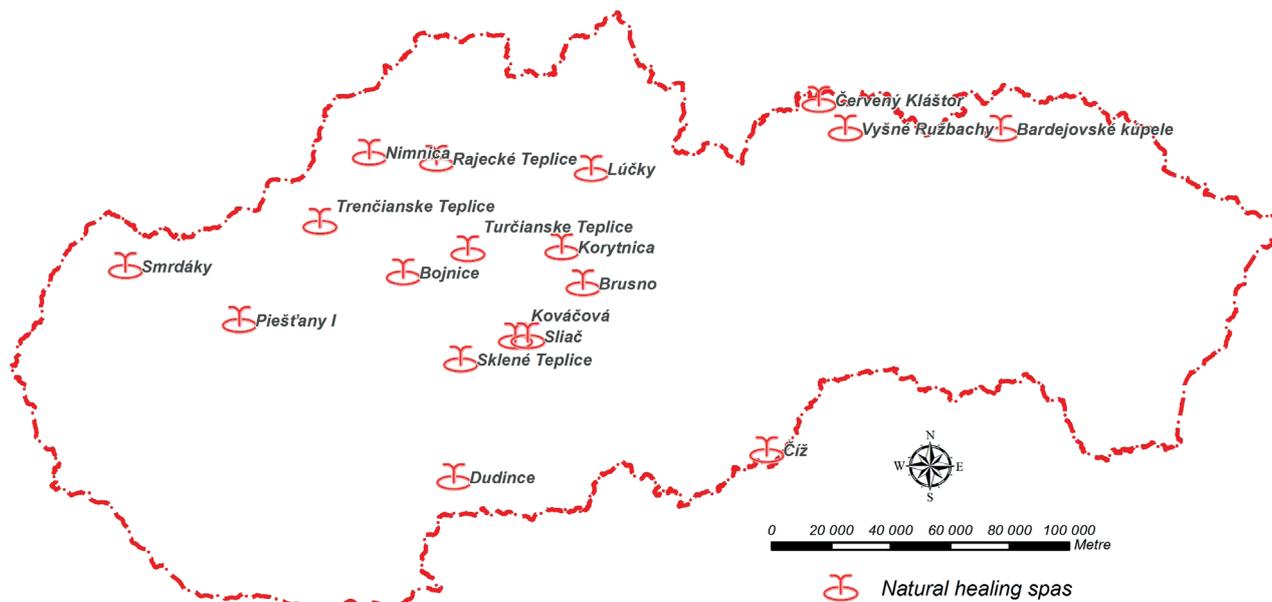


Fig. 3.2 Current spas in Slovakia

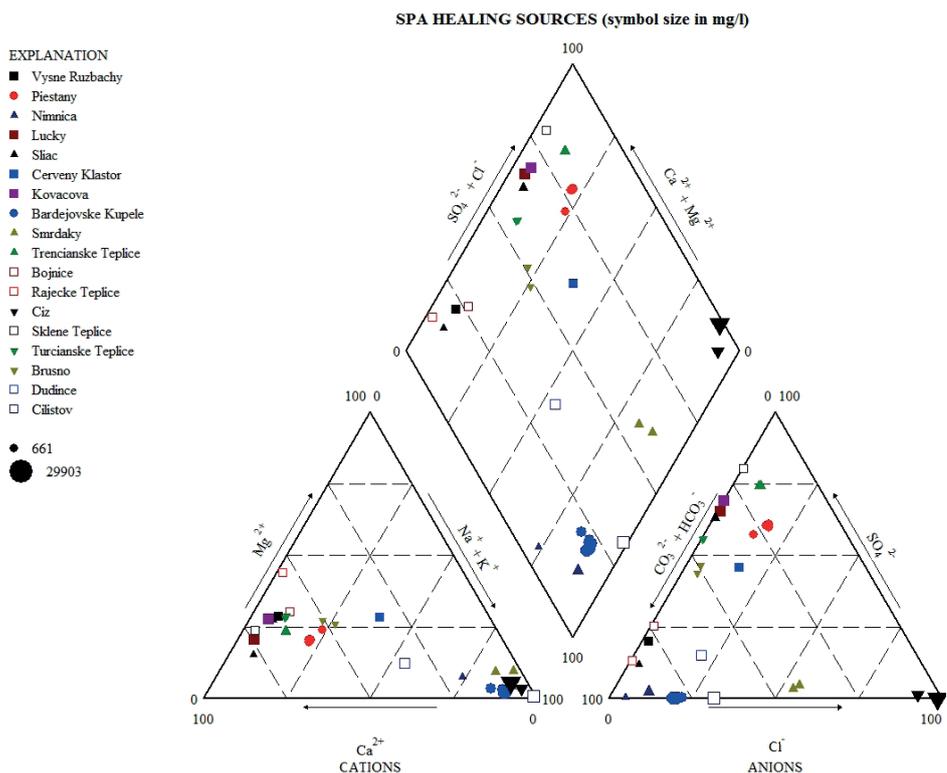


Fig. 3.3 Systemisation of chemical composition of mineral waters of the Slovak spas

The rating is made of a total of 36 chemical analyses. Variety of chemical composition is best documentable by Piper diagram (Fig. 3.3).

Diversity of content of each major ions in the mineral waters of the spas in Slovakia documents the situation of individual points and their projections in a triangular diagrams. They are located at their peaks with maximum representation of ions. Similarly, it is also seen in the central quadrangle, where the projection points are distributed in an area of the peaks. An exemption among the cations is magnesium, which only in exceptional cases exceeds the calcium content in mineral waters, due to interactions with the rock and the prevalent share of limestone in the hydrogeological structures of the spa sources. Similarly to the chemical composition of mineral water, the TDS is in a wide diapason (Fig. 3.2) from 661 mg · l<sup>-1</sup> to 29,903 mg · l<sup>-1</sup>. The lowest values are characteristic for acratotherms (Ražeké Teplice and Bojnice) and the highest ones for somewhat degraded relict marine waters of strong Na-Cl type in Číž.

Basic statistical characteristics of the mineral water of spas is presented in Tab. 3.3. It documents the variability of the components of water and in most cases their uneven distribution. Differences in mean and median, and similarly large differences in minimum and maximum values refer to different natural conditions of the evolution of these waters. In terms of content of gases it can be said that most of the mineral water is oversaturated with gaseous carbon dioxide. The occurrence of hydrogen sulphide is a subject to specific conditions, in which, moreover, biological processes also participate, in this case the desulphurification bacteria. A characteristic example is the Spa Smrdáky. An interesting feature is the presence of both gases in the Dudince mineral water, which can be said world rarity. All components are the products of natural processes, and have evolved in relatively stable conditions mostly in deeper hydrogeological structures for long periods of time. Iron and manganese contents are of natural origin and are typical for most mineral waters of the Western Carpathians. Naturally raised organic matter content, expressed as COD, is characteristic mainly for mineral water of Na-Cl

Tab. 3.3 Main statistical parameters of chemical composition of mineral waters of spas

	Mean	Median	St. dev.	Minimum	Maximum	Lower quartile	Upper quartile
T <sub>w</sub>	32.39	29.60	19.89	11.60	67.20	14.00	46.00
pH	6.77	6.72	0.32	6.20	7.69	6.57	6.89
TDS	4,045.7	2,589.0	5,170.4	661.0	29,903.0	1,432.0	5,143.0
CO <sub>2</sub>	865.89	597.50	883.40	0.00	2,486.88	90.20	1,565.94
H <sub>2</sub> S	29.231	0.036	114.356	0.000	496.000	0.005	5.150
Li	0.758	0.340	0.871	0.009	3.640	0.190	1.250
Na	873.58	95.00	1,874.16	4.20	10,400.00	50.75	1,009.50
K	28.65	21.55	25.10	1.80	131.00	14.00	36.55
NH <sub>4</sub>	4.972	0.425	13.418	0.005	71.300	0.149	3.830
Mg	68.00	48.90	61.01	7.20	350.00	28.75	87.44
Ca	239.71	221.50	175.51	15.10	685.78	110.00	277.88
Sr	6.514	5.616	9.086	0.320	53.900	0.838	9.314
Fe	1.720	0.050	4.543	0.003	24.260	0.014	0.535
Mn	0.212	0.036	0.311	0.001	1.071	0.007	0.417
Ba	0.521	0.070	1.037	0.018	5.190	0.032	0.455
Al	0.054	0.013	0.108	0.000	0.530	0.010	0.046
F	1.54	1.59	1.12	0.05	3.72	0.42	2.10
Cl	916.47	122.50	3,116.36	2.84	17,800.00	16.71	538.50
Br	6.165	0.250	22.945	0.000	120.000	0.100	1.935
I	3.273	0.050	13.606	0.002	76.600	0.025	0.541
HCO <sub>3</sub>	1,363.37	728.00	1,441.13	262.00	4,972.00	407.05	1,810.00
SO <sub>4</sub>	453.22	459.00	483.44	1.80	1,584.70	24.27	582.00
SiO <sub>2</sub>	35.72	29.01	22.87	6.70	108.89	19.35	46.20
COD	3.667	1.115	9.624	0.150	44.300	0.150	2.730

Note: all the data, except T<sub>w</sub> (water temperature °C) and pH are in mg · l<sup>-1</sup>

chemical type, linked mainly to the geochemically and hydrogeologically closed structures. An example provides the already mentioned mineral water in Číž.

At present, it is interesting to know the proportion of species distribution of major and trace elements in mineral water. In the following text there are examples of the value of the total content of selected elements compared to different forms of the element in the complexes and free ions. These findings are relevant in balneology at their behaviour in the human body, but also for the overall characteristics of mineral water and its genesis in sense of modelling of plausible mineral phases in the water-rock-gas interactions.

The above mentioned characteristics of mineral waters were analysed using the code PHREEQC (Parkhurst & Appello, 1999) with a database WATEQ. Background information provided chemical analyses of 36 sources of natural medicinal resources. In the following charts the sites

are listed in number format as follows: 1- Vyšné Ružbachy, 2, 3, 4, 5, 6, 7, 8- Piešťany, 9, 10- Nimnica, 11- Lúčky, 12, 13- Sliach, 14- Červený Kláštor, 15- Kováčová, 16, 17, 18, 19, 20, 21- Bardejovské kúpele, 22, 23- Smrdáky, 24, 25- Trenčianske Teplice, 26- Bojnice, 27- Rajecké Teplice, 28, 29- Číž, 30- Sklené Teplice, 31, 32- Turčianske Teplice, 33, 34- Brusno, 35- Dudince and 36- Čílistov.

Calcium in the mineral waters of the spas occurs mainly as free ion  $\text{Ca}^{2+}$  (Fig. 3.4). The highest percentage (98.5 %) it has in the mineral water source BČ-5 in Číž. The chemical composition of the water, despite the Na-Cl type, reaches one of the highest contents of calcium and magnesium, and sulphates are practically complete absent. The share of complexes  $\text{CaHCO}_3^+$  and  $\text{CaSO}_4^0$  represents the second major calcium species. Their presence practically depends on the representation of bicarbonates and sulphates in mineral waters. In the sulphatogenic waters the complex of  $\text{CaSO}_4^0$  is in prevail (sites Trenčianske

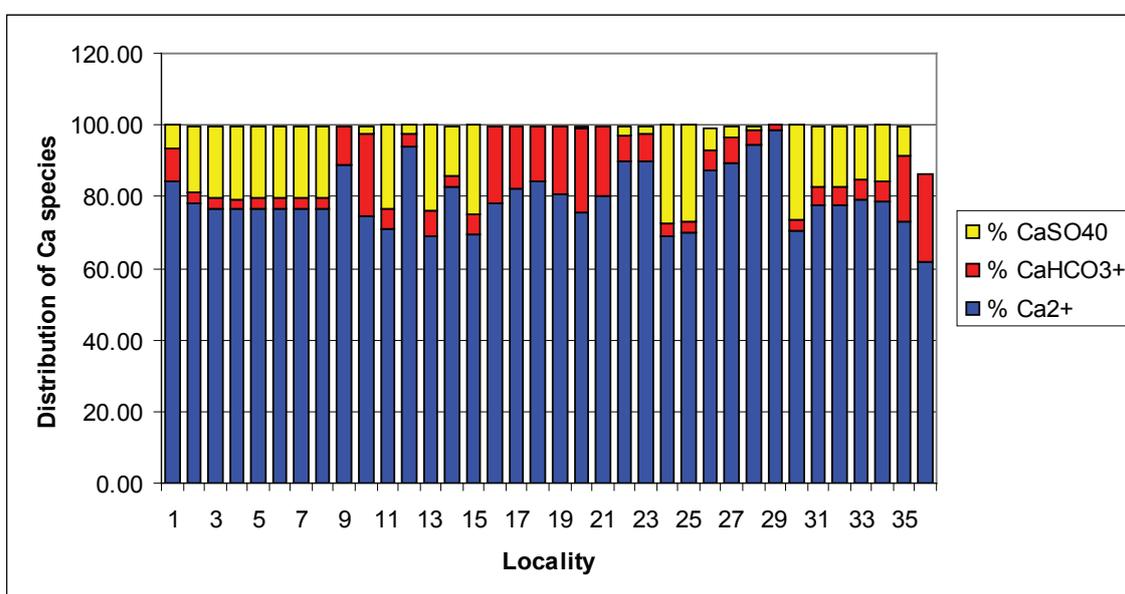


Fig. 3.4 Distribution of calcium species in mineral waters

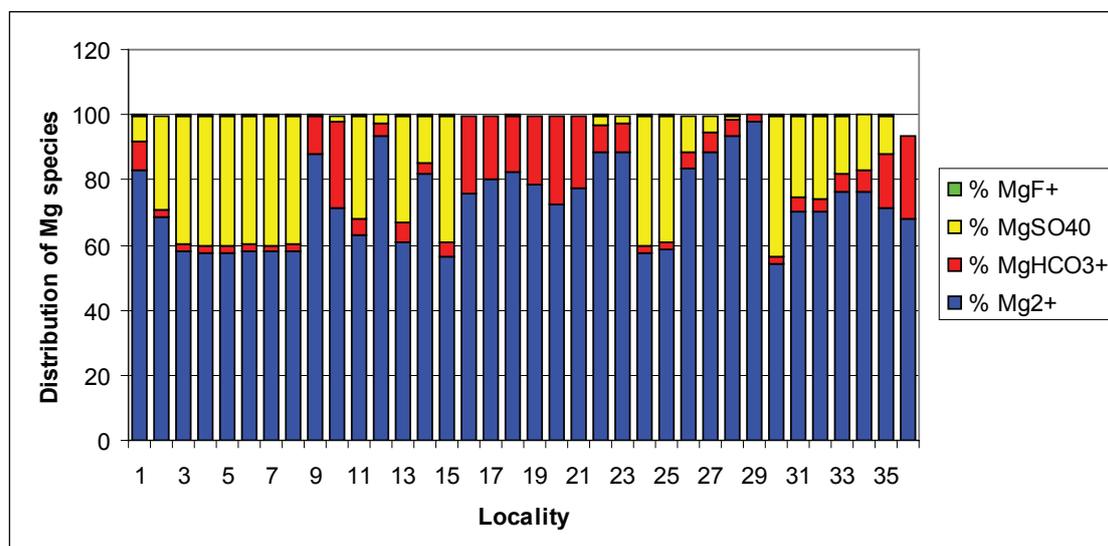


Fig. 3.5 Distribution of magnesium species in mineral waters

Teplice, Sklené Teplice, Kováčová, Sliach and Lúčky) and vice versa  $\text{CaHCO}_3^+$  in mineral waters of Bardejov Spa, Nimnica and Čilistov with  $\text{Na-HCO}_3$  type of waters. Share of the  $\text{CaSO}_4^0$  complex is only 0.03 % in mineral water in Čilistov, where it is also the lowest content of sulphates. The rest (Fig. 3.4) represent a  $\text{CaCO}_3^0$  complex.

Species distribution of magnesium is very similar to calcium by free ion representation, as well as by complexes  $\text{MgHCO}_3^+$  and  $\text{MgSO}_4^0$  (Fig. 3.5). This is due to the similarity of geochemical properties of these two elements and presence, or absence of gypsum/anhydrite in the circulation path of mineral waters. Distribution of the  $\text{MgF}^+$  complex is within the range of 0.01 to 12.52 %, with a maximum in the mineral waters of Piešťany. Similarly to calcium, about 10 % of the magnesium is present in the form of  $\text{MgCO}_3^0$  complex with the occurrence in the water well FGČ-1, Čilistov.

Distribution of potassium and lithium in all mineral waters is mainly represented by free ions of  $\text{K}^+$  and  $\text{Li}^+$ , and in a much lower percentage in complexes  $\text{NaSO}_4^-$  and  $\text{LiSO}_4^-$ .

Bromine in all mineral water of the spas occurs only in the form of the free  $\text{Br}^-$  ion.

Similarly to other waters, the distribution of fluorine species is the subject of their chemical composition and thus their genesis. The highest percentage in the mineral waters of the spas has free ion  $\text{F}^-$ . In most cases it reaches more than 90 % of the amount of fluorine in the water (Fig. 3.6).

The exception is the spring Štefánik (Sliach), which is a mineral water with a low TDS ( $661 \text{ mg} \cdot \text{l}^{-1}$ ), carbonated. It is formed below sedimentary volcanic complexes shallow under the surface. Proof of this is high content of  $\text{SiO}_2$ , up to  $108.89 \text{ mg} \cdot \text{l}^{-1}$ . In addition to the free ion  $\text{F}^-$ , this mineral water contains also the complexes  $\text{AlF}_2^+$ ,  $\text{AlF}_2^+$  and  $\text{AlF}_3^0$ . Different species distribution of fluorine is in mineral water of Brusno with complexes  $\text{AlF}_2^+$ ,  $\text{MgF}^+$ ,  $\text{AlF}_3^0$  and in Dudince with complexes  $\text{MgF}^+$ ,  $\text{AlF}_2^-$  and  $\text{NaF}^0$  (Fig. 3.6).

In most mineral waters silicon is present as undissociated  $\text{H}_4\text{SiO}_4$ . When expressed as a percentage of total silicon it represents more than 99.5 %. The second silicon species

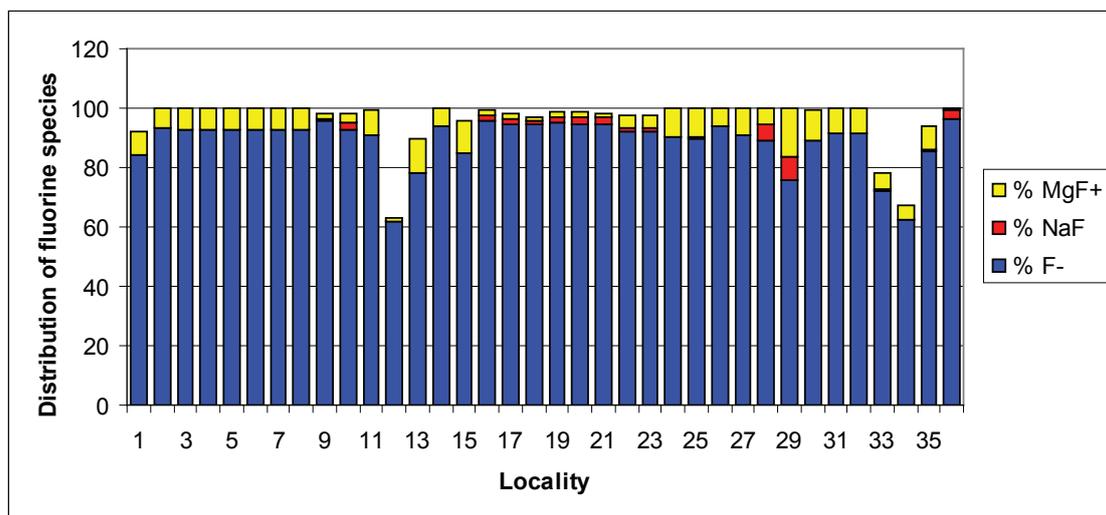


Fig. 3.6 Distribution of fluorine species in mineral waters

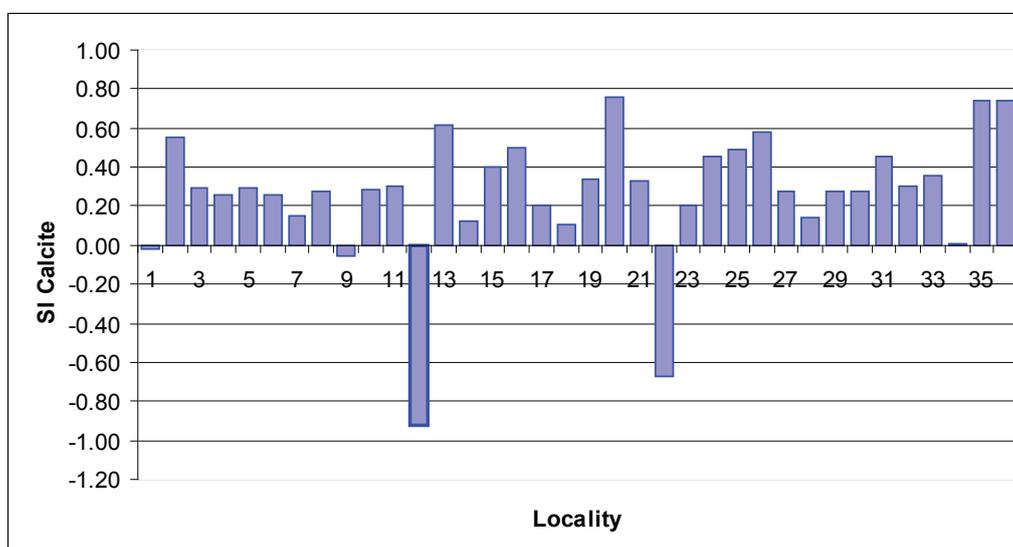


Fig. 3.7 Saturation indices for calcite in mineral waters

in solution is  $\text{H}_3\text{SiO}_4^-$ ; the content is within the range 0.02 to 0.52 %. Interesting case is the mineral water in Čilistov; the said complex silicon reaches 13.2 %. This is probably mainly due to a higher pH (7.69) resulting from absence of carbon dioxide. In general, the concentration of this complex increases with increasing pH of natural waters.

The main mineralization processes in the formation of the chemical composition of mineral waters of the spas in Slovakia are essentially conditioned by two factors. The first one is the source of the elements in the rock environment of the hydrogeological structure. The second are the conditions for the acceleration of geochemical processes, especially temperature, partial pressure of carbon dioxide and water residence time within the collector. Of course, another factor that determines the variety of chemical types of mineral waters in Slovakia, is for example, preservation of relics of sea water and the presence of gas of chemical and biological origin.

It can be stated that in terms of interaction water-rock-gas the most important mineralization process is dissolution of carbonates. This process is the most abundant, or

it affects practically all of the mineral waters. This is also the case where the collectors are not carbonate rocks, e.g. flysch sediments of the Palaeogene and Neogene of the Western Carpathians, which are always to some extent calcareous (calcareous sediments cemented by lime).

The condition of the source of calcium and also magnesium in rock environment of mineral water circulation is met.

The main mineralization processes were evaluated by saturation indices calculated using the code PHREEQC. Steady-states of carbonate minerals dissolution are presented in the examples of calcite, aragonite and dolomite (Figs. 3.7, 3.8, 3.9).

In most of mineral waters calcite is present as supersaturated phase, that means, it will precipitate from the water in the form of carbonate incrusts (Fig. 3.7). In some cases, it has a negative effect in distributors and consumption places (swimming pools and baths) of water. Undersaturated mineral phase is calcite in the cases of Nimnica, Sliac (spring Štefánik) and Smrdáky (Source Josef I). All said mineral waters have the lowest calcium content, which

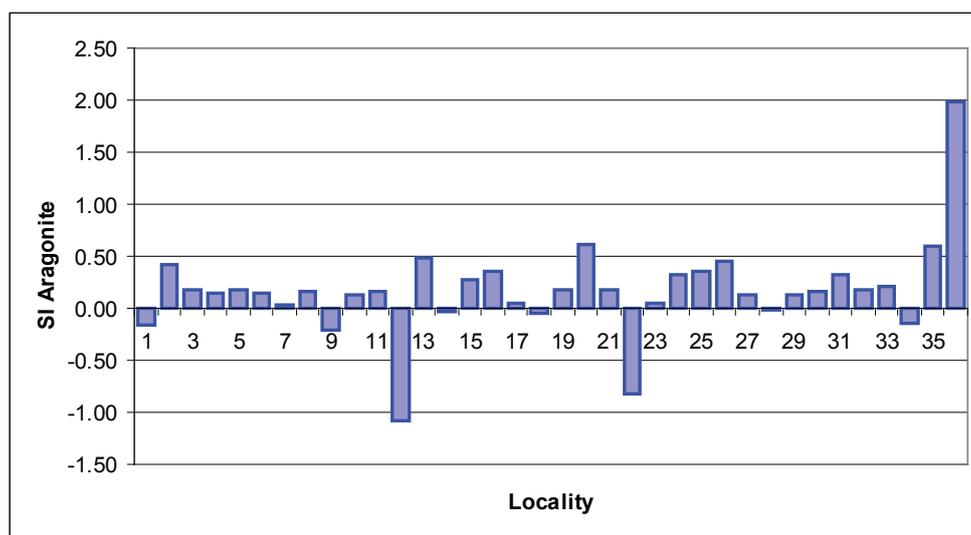


Fig. 3.8 Saturation indices for aragonite in mineral waters

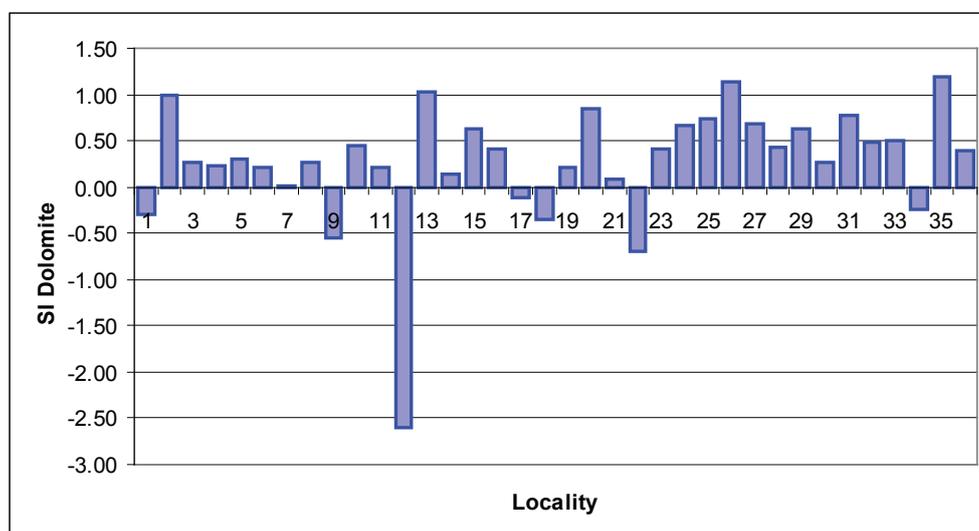


Fig. 3.9 Saturation indices for dolomite in mineral waters

means that within the rock environment of circulation there is no greater source. Mineral phases aragonite and dolomite in the saturation indices exhibit similar behaviour, as well (Figs. 3.8, 3.9).

The second significant mineralization process is the dissolution of gypsum, or anhydrite. From the results of thermodynamic modelling of these mineral phases (Figs. 3.10, 3.11) it follows that all mineral waters are undersaturated against gypsum/anhydrite.

Five sites of mineral water can be assessed to be closer to the equilibrium value of the saturation index, which is  $-0.07 - -0.15$ . These are the sites Sliač (Kúpeľný I.a), Trenčianske Teplice (two sources), Sklené Teplice and Lúčky. The sulphate content of these mineral waters is between  $1,250 - 1,584 \text{ mg} \cdot \text{l}^{-1}$ . Their source of gypsum is present in the Triassic sediments of collectors.

In terms of saturation indices and of the formation of the chemical composition of mineral waters, equilibrium

of mineral quartz is interesting. In most mineral waters chalcedony is supersaturated (Fig. 3.12). Undersaturated phase of chalcedony is in the water of the site Nimnica; the reason is the low temperature as well as low levels of silica in the rock environment circulation. Other location is Ražské Teplice, with a sufficiently high temperature ( $36.4 \text{ }^\circ\text{C}$  at the well head), but the  $\text{SiO}_2$  content in the mineral water is one of the lowest ( $14 \text{ mg} \cdot \text{l}^{-1}$ ), as its formation takes place almost exclusively in the environment of carbonates with limestone dominance.

Amorphous silica is in all mineral waters a undersaturated mineral phase (Fig. 3.13). The exception is the water source Štefánik (Sliač), which, as described above, has the highest content of  $\text{SiO}_2$  of the evaluated mineral waters, thus satisfying the requirements of high silica source in the volcanic rock environment of the chemical composition formation.

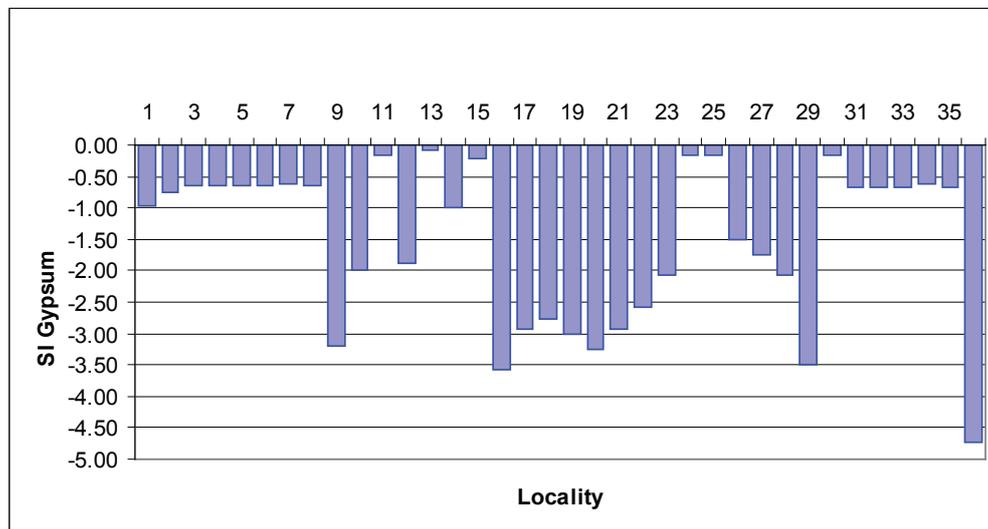


Fig. 3.10 Saturation indices for gypsum in mineral waters

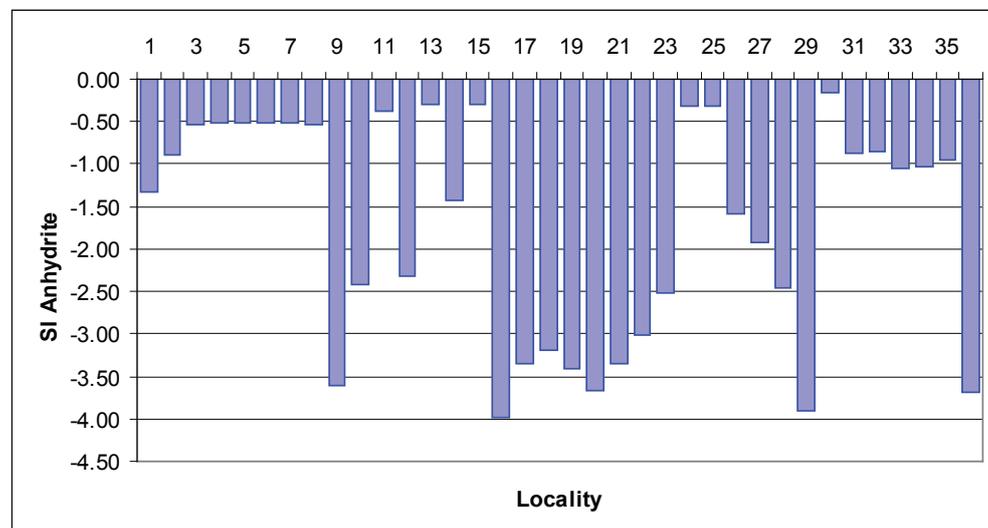


Fig. 3.11 Saturation indices for anhydrite in mineral waters

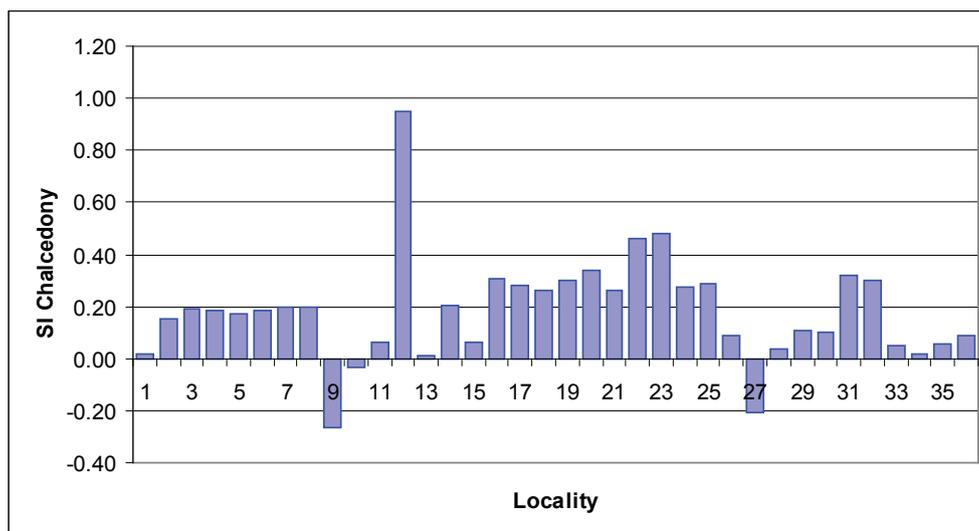


Fig. 3.12 Saturation indices for chalcedony in mineral waters

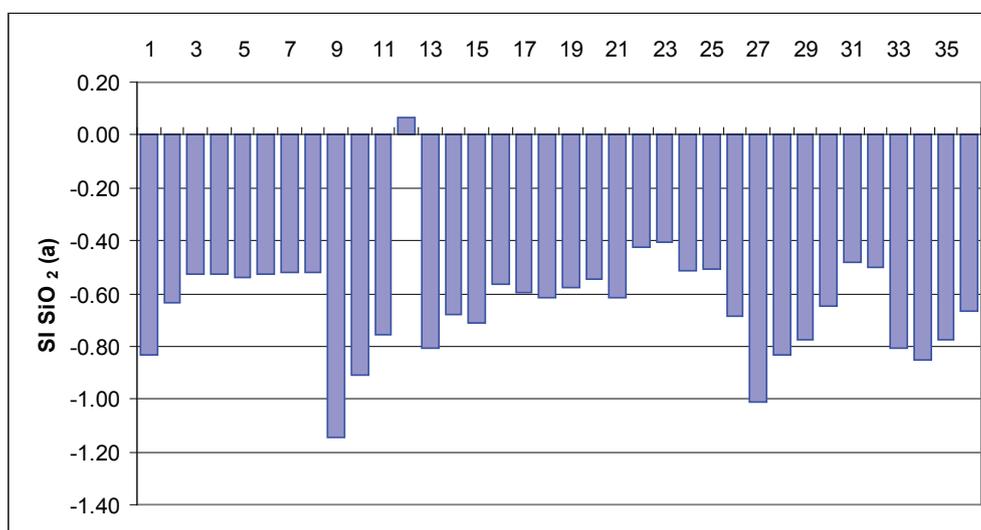


Fig. 3.13 Saturation indices for amorphous SiO<sub>2</sub> in mineral waters

### 3.7 Conclusions

The path of human society to the knowledge of exact values of the chemical composition of mineral water has been very long and lasted for several millennia. Finding of enjoyable and beneficial effects of mineral waters started probably in the form of “try and see”, possibly in hot springs or in its refreshing taste at drinking. During the prevailing alchemy, which extends its beginnings in ancient times and through the entire Middle Ages the composition of mineral water was examined. Epicentre of alchemy was probably China, from where it had spread to India, ancient Egypt, and from there to Greece. In fact, the alchemy did not constitute a science, but philosophy. On the other hand, it should be noted that the period of alchemy was beneficial for modern chemistry for example, by introducing distillation apparatuses, mortar, banks, the development of basic experimental procedures and techniques, and not least the discovery of full range of elements and compounds.

After completing 30 Years' War (1618 – 1648) and its hardships the alchemy experienced decline. This period

can be called transition with regard chemistry as a science. Great advance of the 18<sup>th</sup> Century was the fact, that the issues studied were focused in the problem of combustion, resulting in the so-called phlogiston theory. This theory was introduced by G. E. Stahl, who used also some ideas of his teacher J. J. Becher. In the late 18<sup>th</sup> Century A. L. Lavoisier disproved all the arguments of the phlogiston theory and replaced them with the new one – the theory of oxidation.

Revolution in analytical methods and in the expression of the results of chemical analyses happened at the turn of the 18<sup>th</sup> and 19<sup>th</sup> centuries. The chemical analyses of the early 19<sup>th</sup> Century already examined the contents of the main components expressed in the form of salts. Later, this form of expression changed using the oxides, e.g. CaO, MgO, R<sub>2</sub>O<sub>3</sub>, etc. The current form of expression of the results of chemical analysis in ionic form was introduced at the beginning of the 20<sup>th</sup> Century.

With the development and refinement of chemical analyses of mineral waters it becomes more and more

urgent their evaluation in the classification form. Rather large milestone in the expressing of the chemical composition of water was drawn up in 1864 by Viennese chemist C. Than, who proposed an equivalent form. This was later elaborated by S. Arrhenius, W. Ostwald and others. These authors showed that in aqueous solution the components are not in the form of oxides and salts, as previously believed, but in the form of cations and anions.

The next important factor that influenced the reporting of results of chemical analyses was the elaboration of definition of a system of combining acids (or anions) and bases (or cations). One of the oldest classifications, which is used even today, was invented by Palmer (1911).

Of the current chemical analyses there are presented geochemical characteristics of mineral waters on the basis of 18 spas in Slovakia. By way of examples there are displayed the total contents of selected elements compared to various forms of the element in the complexes. These findings are relevant in balneology at the estimation of their behaviour in the human body, but also for the overall characteristics of mineral water and its genesis within the meaning of modelling of plausible mineral phases in the water-rock-gas interactions.

Calcium in the mineral waters of the spas occurs mainly as free ion  $\text{Ca}^{2+}$ . The highest percentage (98.5 %) it attains in the mineral water source BČ-5 in Číž. The chemical composition of the water, despite the Na-Cl type, is one of the highest contents of calcium and magnesium, in the absence of sulphate. The share of complexes  $\text{CaHCO}_3^+$  and  $\text{CaSO}_4^0$  represents the second major calcium species. The distribution of magnesium species is very similar to calcium in representation of a free ion, as well as complexes  $\text{MgHCO}_3^+$  and  $\text{MgSO}_4^0$ . In all mineral waters distribution of potassium and lithium is mainly represented by free ions  $\text{K}^+$  and  $\text{Li}^+$  and to a much lower percentage in the form of complexes  $\text{KSO}_4^-$  and  $\text{LiSO}_4^-$ . Bromine in all mineral water of the spas occurs only in the form of the free  $\text{Br}^-$  ion. Free  $\text{F}^-$  ion in mineral waters of the spas has the highest percentage representation; in most cases more than 90 % of the amount of fluorine in the water. In most mineral waters silicon is present in the form of un-dissociated  $\text{H}_4\text{SiO}_4$ . These results can be a good basis for balneological evaluation of mineral waters and their effects on the human body.

The main mineralization processes of the formation of the chemical composition of mineral waters of the Slovak spas are essentially conditioned by two factors. The first is the source of the element in the rock environment of the hydrogeological structure. The second are the conditions for the acceleration of geochemical processes, especially temperature, partial pressure of carbon dioxide and water residence time within the collector. Of course, other factors that determine the variety of chemical types of mineral waters in Slovakia, are for example, preservation of relicts of marine water and the presence of gas of chemical and biological origin.

The results of the thermodynamic analysis indicate that, in terms of interaction water-rock-gas the most important mineralization process in the formation of the chemical

composition of mineral waters in the spas is dissolution of carbonates and gypsum sediments of Mesozoic, Palaeogene and Neogene complexes of the Western Carpathians in interaction with carbon dioxide.

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