Abstract

Waters used for hydrotherapy in French medical hydrotherapy centers are legally called Natural Mineral Waters (NMW). Sometimes they are called Thermal Waters but this denomination is little confusing with hot (drinking) waters. There is no legal specific definition of NMW used in spas; the only definition is the European definition for bottled NMW (directive EC 2009/54) which fully applies to spa centers. Natural mineral waters have their own specificity that differentiates them from any ordinary water. A NMW must have properties favourable to health; other requirements are the stability of chemical composition, a groundwater origin and have a great original purity. This is not the chemical composition of the water that determines whether or not it will be classified as mineral water, but the evidence of the therapeutic effectiveness of water according to guideline of Academy of Medicine.

First, water should be characterized and a thorough study of its components done. Such waters are very complex, the various dissolved species remaining in equilibrium each other. It is also clear that some mineral waters, as sulphide waters, chloride waters and sulphate waters, because their components predispose for use in thermal treatment of respiratory or metabolic disorders internal. But it appears only as a presumption of efficiency.

The regulation of mineral waters requires high level of microbiological purity every where in spa centers: the water must be free to all points of use of pathogens (including Pseudomonas aeruginosa and Legionella pneumophila) and the parasites. In case of contamination of any part of the treatment room, local Health Authorities will immediately close it.

Official recognition by local Health Authorities and Academy of Medicine are the guarantee of the therapeutic efficacy of these waters; a strict control of water and sanitation facilities and sooner the certification process of spa therapy centers provide a high level of safety.

Key words: natural mineral waters, control, French medical hydrotherapy centers

Résumé

Spécificité, législation et contrôle des eaux minérales utilisées dans les établissements thermaux français.

La dénomination officielle des eaux exploitées dans les établissements thermaux est l’eau minérale naturelle, celle existant pour les eaux embouteillées. Il n’existe pas de définition
Introduction

There is no legal definition of Natural Mineral Waters (NMW) used in spas except the European definition for bottled NMW (directive EC 2009/54) [1]. French legislation makes no difference between bottled NMW and NMW used in spa therapy; they are legally called Natural Mineral Waters.

Among 700 NMW springs approved in France [2], many are used in both bottling facilities and in spas (for example, Vittel, Saint-Yorre, Evian, Contrexéville, Dax, etc…).

What are NMW’ s and how to characterize them?

The European definition of a NMW is clear:

“Natural mineral water” means microbiologically wholesome water, originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bore exits.

1. Natural mineral water can be clearly distinguished from ordinary drinking water:
   (a) by its nature, which is characterized by its mineral content, trace elements or other constituents and, where appropriate, by certain effects;
   (b) by its original purity,
both characteristics having been preserved intact because of the underground origin of such water, which has been protected from all risk of pollution.

2. The characteristics referred to in point 1, which may give natural mineral water properties favorable to health, shall have been assessed:
(a) from the following points of view:
(i) geological and hydrological,
(ii) physical, chemical and physico-chemical,
(iii) microbiological,
(iv) if necessary, pharmacological, physiological and clinical.”

The approval of a Natural Mineral Water used in spas follows a scheme in 2 steps. Characterisation of NMW is the first step of assessment by checking water characteristics, chemical stability and natural protection of resource, in compliance with technical requirements of European directive.

It should be noted that in the French regulation mineral water is not necessarily mineralized water, following the Latin tradition. Chemical constituents of mineral water confer them “medical interest”[3].

Them, prior approval and use in spa therapy, operator must provide data from clinical trials on individuals, the second step of assessment. “Certain effects” (therapeutic effects in spa therapy) are assessed by French Medicine Academy. Furthermore, French regulation has laid down special provisions for water control facilities and to ensure consistency of chemical quality and microbial safety.

**How to classify NMW?**

The first way is to take into account their chemical composition and, if necessary, their others products (by-products) used such as gas.

The classification should consider physical and chemical parameters that may have “certain effects” [4]:
- temperature,
- pH,
- ions: Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻, HS⁻, Fe²⁺, Mn²⁺, etc.,
- soluble silica H₄SiO₄, expressed in SiO₂,
- gas: H₂S, CO₂,
- or solid phases in suspension.

Total salt dissolved explained as dry residue may be a rough classification [5] including 5 categories between a few milligrams per liter and grams per liter.
- NMW very low mineral content: dry residue < 50 mg/L,
- NMW low mineral content: dry residue > 50 mg/L and < 500 mg/L,
- NMW medium mineral content: dry residue > 500 mg/L and < 1 000 mg/L,
- NMW mineral content: dry residue > 1 000 mg/L and < 1 500 mg/L,
- NMW rich in mineral content: dry residue > 1 500 mg/L

However, mineral content cannot characterize and differentiate between mineral waters because it does not include their chemical profile (called “faciès”) and much less their derivatives such as gas, and/or plankton.

Some chemical elements can justify specific categories.
This is the case of:
• sulphide waters,
• sulphate waters,
• chloride waters,
• natural carbonated waters,
• a combination of sulphate, chloride and hydrogenocarbonate of Na, Ca, Mg.

Mineral waters can have multiple profiles by combining each category. For example, the first 3 categories can exist together, but we shall never meet the first and last. However, waters with an equal distribution between their ionic species do exist and are called “mixed” waters.

It’s the case of weakly mineralized water, containing mainly bicarbonates of calcium and sometimes magnesium.

Main categories of NMW’s

1) Sulphide waters

Sulphide waters are a specific category of water having a particular benefit for the treatment of respiratory diseases.

Little known in their composition until recently, the sulphide waters have sulphur element existing in several oxidation states. Since the most reduced to the oxidized form, respectively, we find the following species [6]:
• sulphides [H₂S], [HS]⁻, [S]²⁻, [RS]⁻ - R is organic radical,
• polysulphides [HS]ⁿ⁻, [Sn]²⁻, n > 1
• elemental sulphur [S₈]
• thiosulphates [S₂O₃]²⁻
• sulphates [SO₄]²⁻

Speciation of sulphur in water

Sulphide waters have a very negative redox potential leading to oxidation-reduction of species. These waters are extremely unstable and combine easily with oxygen, sulphide become either insoluble elemental sulphur (S₈), which appears as yellow particles in swimming pools for example or soluble sulphate. In the presence of organic compounds, sulphides can also form organic sulphides (mercaptans) that are often very fragrant.

Level of sulphides (expressed as [H₂S] = [H₂S] + [HS]⁻ + [S]²⁻ in millimole/liter - mM/L can vary between 0,01 mM/L (respecting 0,3 mg/L) for lowest sulphide waters to 4,3 mM/L (150 mg/L) for highest. Levels lower 0,01 mM/L are not regarded as sulphide water, but as slightly reduced accidental microbial reduction of sulphate to sulphide.

The distribution between the reduced forms of sulphide is related to the pH of the water: in alkaline medium [HS] - and [S] species predominate on the [H₂S] while in neutral medium [H₂S] and [HS] - are predominant, which explains their characteristic odour of hydrogen sulphide - “eggs” - in spas.
Sulphide waters can be classified in two parts:
- **Sodium sulphide waters (called “Pyrenean waters”)** [7]
  
  Such waters are low mineralized (dry residue lower than 400 mg/L), hot (30°C < t < 65°C), alkaline (8 < pH < 10), level of sulphide (0.05 < [H₂S] < 0.4 mM/L - 13.6 mg/L expressed as H₂S), sodium (about 90 mg/L), silica and high level in fluoride (16 mg/L for Amélie-les-Bains waters).
  
  Total silica – partially ionized in ionic form [H₃SiO₄]⁻ due to alkaline pH - can reach 25 % of total salt dissolved.
  
  Example of such “Pyrenean waters”: Luchon, Cauterets, Amélie-les-Bains, ...

- **Calcium sulphide waters** [8]
  
  Such category contains waters having high level of calcium combined with sulphides. Most of them are cold.
  
  Total salts dissolved vary between a few milligrams per liter to many grams. pH of waters is neutral (between 7 and 8) that generate hydrogen sulphide [H₂S]. Calcium is the dominant cation while the dominant anion is sulphate and sometimes chlorides.
  
  These waters are very complex and oxidation can lead to other soluble elements such as sulphates, and insoluble such as elementary sulphur and sometimes carbonate of calcium.
  
  Example of such waters: Aix-les-Bains, Enghien-les-Bains, Allevard, Challes-les-Eaux or les Camoins.
  
  Sulphide waters are used in spas for the properties of hydrogen sulphide, soluble silica and sodium in the treatment of respiratory diseases and dermatology.

2) Sulphate waters

Such waters contain sulphates [SO₄]²⁻ combined with calcium and magnesium coming from dissolution of gypsum content in the deep geological underground. Depending of level calcium/sodium/magnesium, waters are called calcium sulphate waters, sodium (rare in France) or “mixtes” when the mineralization contains a natural mixture of sodium sulphate and chloride.

Solubility of calcium sulphate depends of temperature with the maximum of 38°C. In some calcium sulphate waters, they have a high quantity of natural strontium (till 10 mg/L) and they contain magnesium.

In these category natural mineral waters of Vittel, Contrexéville, Dax, used in urinary tract and metabolic diseases.

3) Sodium chloride waters

Sodium chloride waters contain dominant ion, chloride [Cl]⁻ combined with sodium. They are neither bottled.

These waters are mainly used in rheumatology due to optimum temperature for the human body and a higher density than drinking water. Examples: Balaruc, Amnéville, Salies-de-Béarn, Lectoure or Jonzac.

Two categories can be distinguished:
- Sodium chloride waters: cold and very mineralized
Resulting of dissolution of natural sodium chloride (halite), level of chloride can reach saturation (300 g/L). These waters are very corrosives versus metallic materials and are never used pure in spas.

- Sodium chloride waters: hot and medium or rich mineralized
Total salt dissolved is mainly lower than a few grams per liter and are very corrosives in contact of metallic materials.

4) Natural carbonated (gaseous) waters
All ground waters have hydrogenocarbonates (bicarbonates) [HCO₃⁻] of sodium and dissolved CO₂ in more or less quantity; they could be called “bicarbonate waters”. But dissolved (free) CO₂ provides specific properties that justify a specific category. Denomination “naturally carbonated waters” applies to waters having free CO₂ greater than 250 mg/L, and high level of bicarbonate [HCO₃⁻], generally greater than 1 g/L of [HCO₃⁻].

A distinction should be made between fully equilibrated and non-equilibrated waters but it does not seem to have a real impact for care but only for plants: precipitates of iron, calcium carbonate in swimming pool, networks….

Note that these carbonate anions can interact with the cations present in the water to form insoluble carbonates. pH of theses waters is generally low. Most dominant cation is sodium (quantity higher than 1 gram per liter) and sometimes calcium.

Role of carbonic acid in blood
Carbonic acid is an intermediate step in the transport of CO₂ out of the body via respiratory gas exchange. Carbonic acid also plays a very important role as a buffer in mammalian blood. The equilibrium between carbon dioxide and carbonic acid is very important for controlling the acidity of body fluids.

Example of such waters in Auvergne having high level of bicarbonates of sodium or rich in dissolved CO₂ for diseases of the heart arteries (Royat, le Boulou) or respiratory disease (le Mont-Dore, la Bourboule).

Such waters are rich in fluoride, silica and arsenic.

5) Low mineralized waters
Waters having a low mineral content (lower than 500 mg/L) and without specific chemicals described, no predominant element to identify families earlier.

It is most often low mineralized water, sometimes very weakly mineralized containing tens of milligrams per liter of dissolved solids and calcium bicarbonate type and sometimes magnesium.

In this category we find waters called “trace metal”. The presence of elements such as copper, arsenic, selenium, zinc or vanadium at microgram per liter level was detected by emission spectroscopy and atomic absorption and now by induced coupled plasma mass spectrometry.
It is difficult to attribute at microgram level a specific activity. Yet there are cases where efficiency is clearly demonstrated: selenium in la Roche-Posay water gives good properties in dermatology due to the species of Se (Se³⁺/Se⁵⁺)

6) Ferruginous waters

This is not a particular category because the soluble iron is never the dominant element. Iron and Manganese are always associated with another element (bicarbonate), sometimes several (chlorides and sulphates of sodium and calcium) of the three previous categories. In this case, iron is a sub-category of waters listed above, a bit like water calcium sulphide.

These are waters that contain a soluble, iron, present as [Fe]²⁺ at concentrations varying between 0.5 and 20 mg/L. Examples of such waters: Amneville, Jonzac or Rochefort-sur-Mer. This item is found primarily in deep groundwater, low level of dissolved oxygen and is often associated with low quantity of soluble manganese in the form [Mn]³⁺. Under the action of oxygen from aeration of the water during transportation or storage, these elements are oxidized [Fe]³⁺ or [Mn]⁴⁺ and precipitated as hydroxide of carbonate or iron used mainly as sludge called ferruginous (Salins-les-Thermes).

Regulation of NMW


The purpose of the new regulation is to:
- simplify administrative procedures,
- harmonize procedures by putting a single definition of mineral water whatever its use: spa (hydrotherapy or medical hydrology), bottling, free bar public,
- implement the EU regulations about bottled NMW (technical definition of NMW),
- require the operator to provide evidences that water has the characteristics of natural mineral water,
- implement quality assurance procedures based on HACCP (Hazard Analysis Critical Control Point) principles and best practices in each spas,
- carry out appropriate check monitoring at frequency defined by HACCP studies and content as determined by the rules.

Recognition of new NMW by health authorities: a 2-step procedure

- natural protection of water: geologic and hydrogeological studies,
- protection against surface waters, use of the BAT: Best Available Technology, for capturing water from borehole to uses,
- protection against alteration of properties of water by using assessed materials,
- justification of natural purity and stability of chemical composition: data of 12 microbial analysis and chemical analysis during a year, analysis of radioactivity must be provided.

**Microbial requirements**
At source a natural mineral water shall be free from:
(a) Parasites (*Cryptosporidium* and *Giardia*) and pathogenic micro-organisms,
(b) *Escherichia coli* and other coliforms and faecal streptococci in any 250 mL sample examined,
(c) Sporulated sulfite-reducing anaerobes (*Clostridium perfringens*) in any 50 mL sample examined,
(d) *Pseudomonas aeruginosa* in any 250 mL sample examined,
(e) *Legionella pneumophila* in 1 liter (< of limit of detection of normalized method) [12].

Local Health Authority assesses the technical dossier and gives the permission to use water as NMW.

For use in spas, operator must provide scientific evidence of therapeutic effect in compliance with French Medicine Academy guideline published in 2006 [13].

Dossier including data is then submitted to French Medicine Academy for assessment.

Regulation set up specific requirements concerning use of NMW, depending of uses in a spa [14].

**Water disinfection treatments (27/02/2007 regulation)**
As to bottled NMW, water treatments in spa therapy are authorized under strict conditions: no alteration of the composition of the water as regards the essential constituents, the treatment is notified to, and specifically controlled by the competent authorities:
- the separation of its unstable elements, such as iron and sulphur compounds, by filtration or decanting, possibly preceded by oxygenation,
- the separation of iron, manganese and sulphur compounds and arsenic from certain natural mineral waters by treatment with ozone-enriched air,
- the separation of undesirable constituents other than those specified (example of fluoride),
- the total or partial elimination of free carbon dioxide by exclusively physical methods.

Regulation lays down 4 categories of care for water treatment (Annex 2)
- Type I: direct contact with respiratory mucosa or may cause contact with eye and respiratory mucosa
- Type II: contact with other mucous membranes and internal ingestion of natural mineral water
- Type III: individual care - external body (individual shower or bath), internal mucosa
- Type IV: care Group – swimming pool.

For all other, medical reuse of NMW is prohibited except swimming pool, where persistent disinfectant chemicals such as Chlorine are authorized.
**Official Control**

Regulation set up 3 categories (June 2000) [15] for official control (Annex 3):

*Requirements for each point of use:*

Absence of *Pseudomonas aeruginosa, Legionella pneumophila, E Coli, Cryptosporidium* and *Giardia*

In case of contamination, Health Authority can close part or the whole spa until microbiological compliance.

Natural Mineral Water control is very demanding and ensures a high safety for spa guests. The absence of any pathogen to points of use is a fundamental requirement. This regulation is very burdensome and very costly for operators, since in case of contamination of water in a part of spa, it is immediately closed and disinfected. It also takes into account a policy of quality assurance procedures with many cleaning, disinfecting procedures.

Points of use are defined by Authorities (random) and are specific of a category and tests carried out by accredited laboratories.

*Self controlling*

Operator must define a risk assessment based on Hazard Analysis Critical Control Points (HACCP) principles – a very useful tool in the prevention of food safety hazards:

The HACCP is a system, which identifies, evaluates and controls hazards, which are significant to health safety.

Remind that seven principles of HACCP are:

Principle 1: conduct a hazard analysis. Plans determine any biological, chemical, or physical property that may cause water in spas to be unsafe for human contact;

Principle 2: identify critical control points in NMW process. A Critical Control Point (CCP) is a point, step, or procedure in water process at which control can be applied and, as a result, a water safety hazard can be prevented, eliminated, or reduced to an acceptable level;

Principle 3: establish critical limits for each critical control point;

Principle 4: establish critical control point monitoring requirements. Monitoring activities are necessary to ensure that the process is under control at each critical control point;

Principle 5: establish corrective actions. These are actions to be taken when monitoring indicates a deviation from an established critical limit;

Principle 6: establish record keeping procedures. The HACCP regulation requires that all plants maintain certain documents, including its hazard analysis and written HACCP plan, and records documenting the monitoring of critical control points, critical limits, verification activities, and the handling of processing deviations;

Principle 7: establish procedures for ensuring the HACCP system is working as intended. Tests are carried out by internal or independent laboratory (accredited laboratories).

It should be note that the certification of spas therapy centers is on going: AQUACERT HACCP Thermalisme®, Système de Management de la Sécurité des Produits Thermaux (in compliance with ISO 17021).
Conclusion

Natural mineral waters have their own specificity that leads to differentiate them from any drinking water. A NMW must have properties beneficial to health and meet certain stability requirements of chemical composition, groundwater origin and have a great original purity.

The chemical composition of water does not determine whether or not it will be classified as mineral water, but the clinical dossier assessed according to guidelines developed by the Academy of Medicine.

Natural Mineral Waters are very complex and must be characterized thorough study of their dissolved components.

It is also clear those certain types of mineral waters, as sulphide waters, chloride waters and sulphate waters, because their components predispose for use in thermal treatment of respiratory or metabolic disorders internal. But it appears only as a presumption of efficiency.

Strict control of water and sanitation facilities in their care provides a high level of safety.
ANNEX 1
2 steps of recognition

**THERMALISM**
Recognition of N.M.W
in 2 steps

- **Technical dossier**
  - Compliance with:
    * Requirements of Directive EC 2009/54
    * AFSSA guideline (2008)

- **Local Health Authority Assessment**

- **Spa Therapy**
  - USES

- **Medical dossier**
  - Compliance with 2006 ANM Guideline
    - **Main requirements**
      * Characterisation
      * Water Stability
      * Resource Protection
      * Original Purity
    - **Assessment of French Medicine data by Academy**

- **Recognition by Local Authority = Approval**

AFSSA = French Food Safety Agency
ANM = National Academy of Medicine

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ANNEX 2

*Authorized treatments depending of uses*

<table>
<thead>
<tr>
<th>Category of care</th>
<th>Authorized treatments</th>
</tr>
</thead>
</table>
| **Type I**: Care in direct contact with respiratory mucosa or may cause contact with eye and respiratory mucosa | - Irradiation by U.V just before use  
- Membrane filtration just before use |
| **Type II**: Care in contact with other mucous membranes and internal ingestion of natural mineral water. | - Flash pasteurisation, refreshing just before use |
| **Type III**: Individual patient care (bath) | - Irradiation by U.V just before use  
- Filtration just before use |
| **Type IV**: Collective care (swimming pool) | - Same as for public swimming pools. |

ANNEX 3

*Point of compliance - Parametric values*

<table>
<thead>
<tr>
<th>At spring</th>
<th>Points of use</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
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</thead>
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<td><strong>Coliforms</strong></td>
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<td>Absence</td>
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<tr>
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<tr>
<td><em>Enterococci</em></td>
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<tr>
<td><em>Clostridium perfringens</em></td>
<td>Absence</td>
<td>Absence</td>
<td>Absence</td>
<td>Absence</td>
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<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>Absence</td>
<td>Absence</td>
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</tr>
</tbody>
</table>

CFU = Colony Forming Unit

(1) Care in direct contact with respiratory mucosa or may cause contact with eye and respiratory mucosa.
(2) Care in contact with other mucous membranes and internal ingestion of natural mineral water.
(3) Individual patient care (baths, showers) or group (walking corridor).
Bibliography