



AGENCE FRANÇAISE  
DE SÉCURITÉ SANITAIRE  
DES ALIMENTS

## **Guidelines on the assessment of ion exchangers used for the treatment of water intended for human consumption**

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Requests 2006-SA-0286 and 2006-SA-0350

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## Foreword

Following a proposal by the Scientific panel on Water (CES on Water), AFSSA issued an internal request on 3 October 2006 in order to draft a set of guidelines for the assessment of ion exchangers used for treating water intended for human consumption (Request no. 2006-SA-0286). In addition, the Directorate General for Health (DGS), in a letter dated 7 December 2006, requested AFSSA's scientific and technical support for the updating of guidelines on the assessment of processes using ion-exchange resins for treating water intended for human consumption (Request no. 2006-SA-0350). These requests related to:

- the conditions for examining the chemical formulation of ion-exchange resins, either organic or inorganic (list of chemicals that can be used in the manufacture of resins, etc.);
- the quality of the products used for resin disinfection and regeneration;
- the type of migration tests to be performed, including the water contact conditions for the resins and the parameters to be measured in test water;
- the criteria of acceptability for the resins;
- where appropriate, information on how to assess the effectiveness of the processes or the resin selectivity;
- any other information worthy of special attention when using ion-exchange resins such as, for example, some recommended conditions for using the processes (with regard to resin regeneration or disinfection, minimum water quality to be obtained after treatment, etc.), particularly where resins are to be used by individuals in water distribution systems within buildings;
- the type of information to be provided by anyone overseeing the marketing of resins to potential users of these processes (see Consumer Safety Commission's Opinion of 6 July 2006).

A working group was established by decision of the Director General of AFSSA on 5 December 2006 for a period of 18 months, and its mandate was extended until June 2009. Two meetings were organised with manufacturers of ion-exchange resins.

A hearing with the resin manufacturers took place at the beginning of the mandate, with the aim of gathering information on any practical problems they might have encountered, to enable them to compile their applications and thus obtain approval.

This took into consideration the publication of the European NF EN 12873-3<sup>a</sup> standard defining the water contact conditions for ion-exchange resins and testing them under dynamic conditions, and the present guidelines defining the procedures for implementing this European standard in France.

As the effectiveness of ion-exchange resins depends on their characteristics and exchange capacity as specified by the applicant, no additional expert assessment regarding the effectiveness of the ion-exchange resins was carried out.

The work presented in this report has therefore focused solely on an assessment of the safety aspects of the ion exchangers and the precautions associated with their use.

The findings of the working group were presented to the ion-exchange resin manufacturers on 6 April 2009 and to the experts of the Scientific panel on Water on 7 April 2009. The report was approved by the panel during the 5 May 2009 session.

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<sup>a</sup> NF EN 12873-3 Standard of June 2006: Influence of materials on water intended for human consumption – influence due to migration – Part 3: Test method for ion exchange and adsorbent resins

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## Definitions and glossary

**Affinity – Selectivity coefficient:** a resin's affinity with the different ions determines its selectivity. The selectivity coefficient (usually denoted by  $\alpha$ ) depends on interactions between the ions (mainly related to their charge and their hydrated ionic radius) and the functional groups of the resins. [Fr. Affinité]

**Bed:** quantity of ion exchange material placed in a column. [Fr. Lit]

**Bed volume:** volume occupied by the bed (granular material). [Fr. Volume du lit]

**Brine:** concentrated salt solution with concentration higher than 3.5% by weight, i.e. more concentrated than sea water. As an example, sodium chloride is used for regenerating ion exchangers used for softening. [Fr. Saumure]

**Clinoptilite (Clinoptilolite):** natural zeolite that is selective, particularly of ammonium ions. [Fr. Clinoptilolite]

**Co-current:** term describing an exchanger in which the regenerating agent (or the rinse water) percolates during the regeneration (or rinsing) phase in the same direction as the water to be treated during the exhaustion phase. [Fr. Co- courant]

**Control water:** water which has only been in contact with the test bench used for the migration tests, and not with the exchanger. [Fr. Eau témoin]

**Counter-current:** term describing an exchanger in which the regenerating agent (or the rinse water) percolates during the regeneration phase in the opposite direction to that of the exhaustion phase. [Fr. contre-courant]

**Cycle:** series of operations conducted on an exchanger, beginning at a certain state and returning to an identical state. An exchanger's operating cycle corresponds to a exhaustion phase then a regeneration phase. In practice, the term 'cycle' is often used for the exhaustion phase alone. [Fr. Cycle]

**Exhaustion:** phase during which the ions to be eliminated are bound by the exchanger while the fluid to be treated percolates through the exchange bed. This phase corresponds to the exchanger's production period. [Fr. Epuisement]

**Displacement:** elimination of an ion bound to the resin by an ion whose affinity is greater (stoichiometric exchange). [Fr. Déplacement]

**Distribution coefficient:** ratio of the concentrations, measured at equilibrium, between the exchanger and the water for a given ion. [Fr. Coefficient de partage]

**Elution:** elimination of an ion bound to the resin by an ion whose affinity is lower, but whose concentration is high. [Fr. Élution]

**Exchange capacity:** number of exchange sites in milliequivalents (mEq) or equivalents (Eq) per unit of mass (or volume) of resin (mEq/g, Eq/kg, Eq/L). [Fr. Capacité d'échange]

**Exchange constant:** ratio of the distribution coefficients for the exchanged ions, between the exchanger and the water, at equilibrium. [Fr. Constant d'échange]

**Exchange front:** change in saturation in the case of displacement (exhaustion). [Fr. Front de permutation]

**Formulation:** in the case of an organic or inorganic material, the formulation comprises all the chemical substances, including commercial products, used in the material's initial composition (qualitative and quantitative) and those used during the manufacturing process until the finished product is obtained. [Fr. Formulation]

**Ion exchanger:** insoluble, granular, organic or inorganic material whose structure contains cation-exchange or anion-exchange functional groups and which is liable to exchange ions in the fluid with which it is in contact. This exchange enables the composition of the treated fluid to be altered. [Fr. Échangeur d'ions]

**Material:** component of a finished product, consisting of a basic part having no water treatment function. It is characterised by its trade name and generic name in the case of metals or minerals, or by its trade name and formulation for organic materials (organic polymers, rubber- or silicone-based elastomers, etc.). [Fr. Matériau]

**Migration:** the process by which a substance from the tested element is transferred into water. [Fr. Migration]

**Permutation:** stoichiometric exchange of one ion with another, between the exchanger and the solution. [Fr. Permutation]

**Positive reference lists:** lists of chemicals that can be used to manufacture a material or object coming into contact with water intended for human consumption. Substances not appearing on any of these lists must not be used. [Fr. Listes positives de référence]

**Regeneration:** operation performed on a saturated ion exchanger to restore it to its original state by circulating an appropriate solution, in either a co-current or counter-current direction, within the exchanger.

**Regenerating agent:** reagent used to ensure regeneration. [Fr. Régénération]

**Resin:** generic term for the granular organic materials used in ion exchange. [Fr. Résine]

**Softening:** treatment in which calcium and magnesium are exchanged with sodium. [Fr. Adoucissement]

**Test water:** water which has been in contact with the ion exchanger samples during migration tests. [Fr. Eau d'essai]

**Zeolite:** generic term for the silicoaluminates used as ion exchangers. [Fr. Zéolithe]

## Abbreviations

**ACS:** Health Compliance Certificate (*Attestation de Conformité Sanitaire*)

**AFNOR:** French Standards Institute

**AFSSA:** French Food Safety Agency

**BV:** Bed Volume

**CSHPF:** French High Council for Public Health

**CSP:** French Public Health Code (*Code de la Santé Publique*)

**DVB:** Divinylbenzene

**EN:** European Standard

**EVB:** Ethylvinylbenzene

**FASS:** Flame Atomic Absorption Spectrometry

**GC/MS:** Gas chromatography/Mass spectrometry

**GF/AAS:** Graphite Furnace Atomic Absorption Spectrometry

**HETP:** Height Equivalent to the Theoretical Plate

**ICP-AES:** Inductively Coupled Plasma-Atomic Emission Spectrometry

**ICP-MS:** Inductively Coupled Plasma – Mass spectrometry

**IUPAC:** International Union of Pure and Applied Chemistry

**IZA:** International Zeolite Association

**LC/MS:** Liquid chromatography/Mass spectrometry

**NF:** French Standard

**pH:** potential of Hydrogen

**SML:** Specific migration limit (in food or in the simulator fluid)

**TOC:** Total Organic Carbon

## Introduction

Water intended for human consumption is a vital nutrient. As such it must be continually distributed in sufficient quantity and of the best possible quality. It may be consumed by the general population and is subjected to special purification treatments which evolve as innovations are introduced. These innovations can address health and technical problems, although their efficacy and safety must be ascertained by verifying that they do not degrade the water's organoleptic, chemical and/or microbiological qualities.

Ion-exchange resins have long been used for purifying drinking water and the first approvals for their use in the treatment of water intended for human consumption were issued by the Ministry for Health in the 1990s. They are also being used increasingly in the privately-owned sections of domestic water distribution systems. The best-known processes using ion exchangers are softening, decarbonation and nitrate removal. Other specific exchangers have also been developed, for instance for eliminating boron.

The regulations on ion-exchange resins are currently specified in two circulars dating from 1985<sup>a</sup> and 1987<sup>b</sup>. The Ministerial Order of 29 May 1997<sup>c</sup> (as amended), in its Annex IV, specifies the components authorised for their manufacture. The safety tests on ion-exchange resins, conducted under static conditions, are derived from those used to assess the safety of the materials used for pipes, tanks and seals.

Since its inception, AFSSA has been responsible for the scientific and technical assessment of marketing authorisation applications for treatment products and processes used for water intended for human consumption in France. With the amendment of Articles R.1321-1 *et seq.* of the Public Health Code, the assessment of the safety and efficacy of innovative treatment products and processes is based on an application file containing the elements defined in the Ministerial Order of 17 August 2007<sup>d</sup> (as amended). With the experience it has gained from previous ion exchanger approval applications, AFSSA is proposing in this report a set of guidelines for their assessment. To this end, it has established a working group which has been instructed to improve the current provisions, adapt them to the European context and update the procedure in light of current scientific and analytical elements.

This report sets out the conditions for assessing the safety of ion exchangers. Their application should ensure that henceforth AFSSA's opinion is only sought for particularly specific or complex applications. It should also facilitate the marketing of ion exchangers used for the treatment of water intended for human consumption, while maintaining a high level of safety.

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<sup>a</sup> Circular DGS/DGE/1.D./1135 of 23 July 1985 on the use of anion-exchange resins for the treatment of water intended for human consumption.

<sup>b</sup> Circular DGS/SP5546/10041 of 27 May 1987 on the use of cation-exchange resins for the treatment of water intended for human consumption.

<sup>c</sup> Ministerial Order of 29 May 1997 on the materials and objects used in permanent installations for the production, treatment and distribution of water intended for human consumption.

<sup>d</sup> Ministerial Order of 17 August 2007 on the compilation of the marketing authorisation application for a product or treatment process for water intended for human consumption (*amended by the Ministerial order of 4 June 2009*).

# 1 General aspects of ion exchange and use of ion exchangers in water treatment

## 1.1 Ion exchange and the main types of ion-exchange resins

An ion exchanger is an insoluble, granular, organic or inorganic material to which ion exchanger functional groups are bound. Ion exchange then consists in replacing, by permutation, the ions found in the solution in contact with the ion exchanger, with those bound to the functional groups. This exchange can alter the composition of the fluid in contact with the exchanger and thus performs the treatment.

There are several different kinds of exchanger, the most widespread on the industrial scale being synthetic resins, which, depending on their type, are used for different treatments such as softening, decarbonation, demineralisation or elimination of  $\text{NH}_4^+$  ions.

In general, ion exchangers are characterised by:

- their selectivity, i.e. the relative affinities of different ions for the treatment medium,
- their distribution coefficient, i.e. the ratio of the concentrations, at equilibrium, between the exchanger and the water for a given ion.

More detailed information on the various types of ion exchangers, their operating principles and characteristics, are given in Annex A.

## 1.2 Use of ion exchangers

When an ion exchanger is exhausted or saturated, its binding capacity falls to zero. The ion exchanger must then be returned to its original ionic form so that it can be reused for a new cycle. This is the regeneration sequence, which involves shifting the chemical balance by providing a high concentration of the ion to be exchanged in the subsequent cycle ( $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$  or  $\text{Cl}^-$ ). To do this, a chemical carrier of this ion is used: the regenerating agent (sodium chloride for  $\text{Na}^+$  and  $\text{Cl}^-$ , a mineral acid for  $\text{H}^+$ , caustic soda for  $\text{OH}^-$ ).

### 1.2.1 Operating cycle of a regenerable ion exchanger

There are four phases in an ion exchanger's operating cycle:

- **saturation (production/useful phase):** the solution passes through the exchange bed (downward current) until the bed is saturated. At the leakage point (when the leakage threshold value has been reached), the production phase is stopped.
- **decompacting:** this phase serves to eliminate particles that have been deposited on the surface of the bed, using an upward current of water.
- **regeneration:** this occurs when a regenerating solution is introduced by percolation (upward in the case of a counter-current, downward in the case of a co-current). Depending on the exchanger type and the ions exchanged, the regeneration process will involve elution or displacement. Table 1 gives a list of the most widely used regenerating products.
- **rinsing:** during this phase, the excess regenerating agent found in the water is eliminated at low speed until there are only small traces of regenerating agent left in the resin: this is the slow rinsing phase. This is followed by a rapid rinsing stage whose faster rate removes the last traces of regenerating agent.

**Table I: Most widely used regenerating products**

|                         | Sodium chloride                                                                                     | Hydrochloric acid                                                              | Sulfuric acid                                                                             | Soda                                                                          | Carbonic acid                               |
|-------------------------|-----------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|---------------------------------------------|
| Formula                 | NaCl                                                                                                | HCl                                                                            | H <sub>2</sub> SO <sub>4</sub>                                                            | NaOH                                                                          | H <sub>2</sub> CO <sub>3</sub>              |
| Molar mass              | 58.5                                                                                                | 36.5                                                                           | 96                                                                                        | 40                                                                            | 62                                          |
| Available forms         | Pellets                                                                                             | Solution                                                                       | Solution                                                                                  | Pellets<br>Caustic soda                                                       | Gas dissolved in water                      |
| Solubility in water     | 306 g/L at 20°C                                                                                     | 33 to 35% HCl<br>i.e. 380 to 410 g/L                                           | 92 to 98%<br>i.e. 1.7 to 1.8 kg/L                                                         | 800 g/L<br>(flakes)                                                           | Solution in water depending on the pressure |
| Use with ion exchangers | Strong cation-exchange resins in Na <sup>+</sup><br>Strong anion-exchange resins in Cl <sup>-</sup> | Strong cation-exchange resins in H <sup>+</sup><br>Weak cation-exchange resins | Strong cation-exchange resins in H <sup>+</sup> (risk of CaSO <sub>4</sub> precipitation) | Strong anion-exchange resins in OH <sup>-</sup><br>Weak anion-exchange resins | Weak cation-exchange resins                 |
| Observations            | Salt is neutral: its use is non-hazardous                                                           | Fuming acid<br>Corrosive vapours<br>its use is hazardous                       | Very hazardous acid<br>Sharp rise in temperature on dissolution                           | Very hazardous base                                                           | Weak acid not very hazardous                |
| Use                     | Domestic and industrial use                                                                         | Industrial use                                                                 | Industrial use                                                                            | Industrial use                                                                | Industrial use                              |
| Standard of purity      | NF EN 973                                                                                           | NF EN 939                                                                      | NF EN 899                                                                                 | NF EN 896                                                                     | NF EN 936                                   |

### 1.2.2 Disinfection

Ion exchangers are liable to trap particles suspended in the water that passes through them. Moreover, the exchangers are potential media for the colonisation of bacteria. In the event that contaminated water passes over an ion exchanger, the exchanger may therefore temporarily trap microorganisms, some of which can colonise the surfaces to form a biofilm.

While the exchangers are operating, these microorganisms can foul them and interfere with their functioning. However, the regeneration conditions and the physico-chemical properties of the regenerating products (a highly acidic or highly alkaline medium) mean that bacterial growth will be limited.

Shutting down an ion exchanger for a prolonged period of time promotes bacterial growth, so it is necessary, after a contamination episode in the system or after a prolonged shutdown, to disinfect the ion exchangers. However, in the case of a system contaminated by *Cryptosporidium*, the effectiveness of disinfection is unproven and AFSSA recommends changing or regenerating the resin, for at least one cycle, before using the treated water<sup>e</sup>.

<sup>e</sup> AFSSA Scientific and Technical Support of 19 August 2009 on the health risks associated with the use of softeners and collective and individual water heaters when a distribution system is contaminated by *Cryptosporidium* (No. 2003-SA-0337)

When disinfecting, ion exchanger manufacturers generally advocate carrying out regeneration at the same time. Table II specifies the disinfectants currently recommended.

**Table II: Types of disinfectants currently recommended by manufacturers**

|                    | Hydrogen peroxide             | Peracetic acid                                                               | Sodium hypochlorite             | Calcium hypochlorite  | Hypochlorite obtained by electrolysis of a NaCl solution |
|--------------------|-------------------------------|------------------------------------------------------------------------------|---------------------------------|-----------------------|----------------------------------------------------------|
| Formulation        | H <sub>2</sub> O <sub>2</sub> | CH <sub>3</sub> -COOOH                                                       | NaClO                           | Ca (ClO) <sub>2</sub> | NaClO                                                    |
| Molar mass         | 34                            | 76.1                                                                         | 74.5                            | 142.99                | 74.5                                                     |
| Available forms    | Solution                      | Solution (always sold in combination with acetic acid and hydrogen peroxide) | 10-30% active chlorine solution | Granules              | Solution                                                 |
| Standard of purity | EN 902                        | No specific standard                                                         | NF EN 901                       | NF EN 900             | NF EN 973<br>Standard of purity for sodium chloride      |

### 1.3 Examples of ion exchanger applications in water

#### 1.3.1 Softening (Ca<sup>2+</sup>/Na<sup>+</sup> permutation)

Softening is the most common application for the treatment of water intended for human consumption. It usually involves replacing the alkaline-earth ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>) with alkali ions (Na<sup>+</sup>), as the alkaline-earth ions cause the deactivation of detergents and soaps through complexation, and the scaling of boilers through precipitation of carbonates.

Softening is carried out on a strong acid resin in Na<sup>+</sup> form according to the equilibrium:



where the subscript (r) indicates the ion bound to the resin and the subscript (s) is the one in solution. When the equilibrium shifts to the right, the Ca<sup>2+</sup> ions bind themselves to the resin and the Na<sup>+</sup> ions pass into the solution.

To regenerate the resin, the equilibrium must be shifted to the left, which requires the use of a saturated solution of sodium.

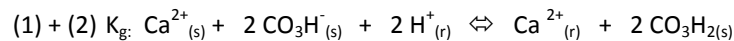
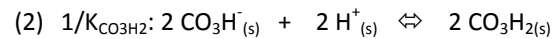
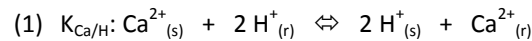
#### 1.3.2 Decarbonation (Ca (CO<sub>3</sub>H)<sup>+</sup>/H<sup>+</sup> permutation)

On weak acid resins (carboxylic exchangers, etc.) the bonds with the ions are covalent and not electrostatic as with strong acid resins (sulfonic acid exchangers). Although there is no well-defined distance for the electrostatic bonds, the same is not true for the covalent bonds. Therefore, a divalent ion such as Ca<sup>2+</sup> will deploy two bonds on a sulfonic acid resin, but will be unable to do this with a carboxylic resin<sup>f</sup>. It therefore follows that on a carboxylic resin, the Ca<sup>2+</sup> ion binds itself to a single site, bringing with it one anion, most often CO<sub>3</sub>H<sup>-</sup>, which is the commonest anion in hard water. Thus it is the Ca (CO<sub>3</sub>H)<sup>+</sup> complex which binds itself to the resin. Simultaneous with the softening, therefore, decarbonation also takes place.

<sup>f</sup> for this, it would be necessary for the bond distances to correspond exactly to the distance between two active sites, which is not the case.

On a weak acid resin, the  $H^+$  ions are more firmly bound than the  $Ca^{2+}$  ions. Thus regenerating a carboxylic resin using a strong acid is very easy as it involves displacement and no excess acid is necessary, unlike the regeneration of a sulfonic acid resin using  $Na^+$  ions which have a lower affinity than  $Ca^{2+}$ . In this case, elution takes place. With regard to the bond, it should not normally be formed if there is no shift in equilibrium due to the presence of the weak base  $CO_3H^-$ .

Consider the following equilibrium equations, where the subscript (s) corresponds to the ions in solution and the subscript (r) to the ions bound to the resin:



The exchange constant  $K_{Ca/H}$  is around  $10^{-3}$  (negative log), i.e. equation (1) is usually shifted to the left and the  $Ca^{2+}$  ions are much less firmly bound than the  $H^+$  ions. However, the global constant  $K_g$  is equal to  $K_{Ca/H} / K_{CO_3H_2}$  i.e. around  $10^{-3} / 10^{-6.4}$  (positive log) and equation (1) + (2) is shifted to the right and the number of  $Ca^{2+}$  ions bound on the resin is very high (greater than 99.9%).

It therefore follows that the  $Ca^{2+}$  bond on a carboxylic resin can only be formed in the presence of  $CO_3H^-$ , which is often the case for natural hard waters, with a temporary elimination of the hardness.

## 2 Regulatory context

The marketing of products and processes for treating water intended for human consumption on the one hand, and their use in permanent water production and distribution plants on the other hand, are subject to regulatory provisions. The ion exchangers used for the treatment of water intended for human consumption are concerned by these provisions.

In addition, all materials and objects used in connection with the use of ion exchangers designed for treating water intended for human consumption must comply with the regulatory requirements in force. An overview of these regulations is given in Annex B.

### 2.1 Conditions for the marketing and use of products and processes for treating water intended for human consumption

#### 2.1.1 Marketing of products and processes for treating water intended for human consumption

As with any materials and objects coming into contact with water intended for human consumption, and in accordance with the provisions of the French Consumer Code<sup>g</sup>, anyone overseeing the marketing of such products is required to ascertain that they are suitable for their intended use, that they comply with the regulations in force and that they are not liable to constitute a danger to consumer health.

In accordance with the provisions of Article R.1321-50 of the French Public Health Code (CSP), *“the treatment products and processes on the market and intended for treating water intended for human consumption must, under the normal or foreseeable conditions of their use, comply with the specific provisions laid down by Order of the Minister for Health to ensure that:*

- *they are not liable, either intrinsically or through their residues, to present a direct or indirect danger to human health or to bring about an alteration in the water composition defined by reference to values set by this Ministerial Order;*
- *they are sufficiently effective.”*

Ministerial Orders, made in application of Articles R.1321-50-I and II of the CSP, will determine the specific provisions relating to the treatment products and processes, according to the groups to which they belong and their uses. These orders will also establish the conditions for certifying compliance with these provisions, which may be effected, depending on the groups and the uses:

- either by whoever oversaw the market launch of the product or treatment process;
- or by a laboratory authorised by the Minister for Health<sup>h</sup> in application of Article R\*.1321-52 of the CSP.

However, in the event that a corporation wishes to market a treatment product or process which does not correspond to any of the groups or uses provided for under Article R.1321-50-I of the CSP, the corporation must comply with the provisions of Article R.1321-50-IV of the aforementioned Code, which corresponds to products or processes considered as ‘innovative’ and not meeting the general duty of compliance, and which may require a higher level of expert assessment and safety. This corporation must then send the Ministry for Health a file containing proof of the safety and efficacy of the product or process. To be admissible, this file must include the information specified in the Ministerial Order of 17 August 2007<sup>d</sup> (as amended). This proof must be provided by whoever oversaw the market launch of the product or process. When requested by the Ministry for Health and based on the file it has been sent, AFSSA shall issue an opinion on the proof that has

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<sup>g</sup> Articles L.121-1 and L.212-1 of the French Consumer Code

<sup>h</sup> The list (in French) of authorised laboratories is available on the Ministry for Health’s website: [www.sante.gouv.fr/htm/dossiers/eaux\\_alimentation/materiaux/liste\\_lab0.pdf](http://www.sante.gouv.fr/htm/dossiers/eaux_alimentation/materiaux/liste_lab0.pdf)

been provided on the safety and efficacy. In the absence of a favourable opinion from AFSSA, the marketing of the water treatment product or process is prohibited.

### **2.1.2 Use of products and processes for treating water intended for human consumption**

Article R.1321-51 of the CSP stipulates that *“the person responsible for the production, distribution or packaging of any water, other than ‘spring water’, shall use products and processes for treating water intended for human consumption, in accordance with the provisions of Article R. 1321-50. For ‘spring water’, the applicable provisions are those of Article R. 1321-85”*.

Anyone overseeing the marketing of a product or process for treating drinking water must therefore:

- offer products or processes that comply with the specific regulatory provisions for the group of products or processes to which it belongs;
- ensure, prior to its market launch, that it complies with the relevant specific provisions;
- send to the authorities and make available to its customers proof of the safety of the product or process, certifying its compliance with the specific provisions.

The provisions of the CSP apply, according to each party’s area of responsibility:

- to manufacturers marketing products or processes for treating drinking water, as well as operators (resellers, assemblers, etc.);
- to persons responsible for the production, distribution and packaging of water.

These provisions apply to all products and processes used, or liable to be used, for the treatment of water intended for human consumption:

- in public distribution systems, from the water intake point in the natural environment to the connection points of subscribers (including storage pools);
- in systems within buildings, including in hot water distribution systems.

### **2.1.3 Specific provisions and proof of compliance relating to groups of water treatment products and processes**

To date, many groups of products and processes for treating water intended for human consumption have been identified. Pending the publication of the Ministerial Orders listed in Article R. 1321-50 of the CSP, the specific provisions to be complied with for certain groups of treatment products and processes have been defined in a number of circulars, in particular Circular DGS/VS4 no. 2000-166 of 28 March 2000 relating to products and processes for the treatment of water intended for human consumption.

## **2.2 Specific provisions relating to ion exchangers for the treatment of water intended for human consumption**

### **2.2.1 Existing provisions**

Water treatment technologies based on ion exchange have been in use for a very long time. Marketing such technologies for the treatment of water intended for human consumption falls under the provisions of Article R.1321-50 of the CSP.

The procedure for assessing safety is based on a procedure adapted from those used to test water contact materials (XP P41-250<sup>i</sup>). It is conducted on the basis of an application for approval of the resin, sent to the Minister for Health by whoever is overseeing its marketing, accompanied by a technical file whose content is specified in the aforementioned Circulars of 23 July 1985 and 27 May 1987. AFSSA is entrusted with assessing

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<sup>i</sup> AFNOR standard XP P41-250-1 Effect of materials on the quality of water intended for human consumption – Organic materials – Part 1 from December 2001: Measurement method for the organoleptic and physico-chemical parameters; Part 2 from December 2001: Method for measuring mineral and organic micropollutants; Part 3 from April 2003: Method for measuring cytotoxicity

these applications, in accordance with the provisions of the Circular of 30 December 2003<sup>j</sup>. Since its inception, AFSSA has issued 43 opinions, of which 27 were favourable, and has expressed an opinion on 37 different ion-exchange resins.

An application for approval shall include:

- an examination, conducted by a laboratory authorised by the Ministry for Health, of the chemical formulation (composition and constitution) of the materials used to manufacture the ion exchanger. This examination is conducted under the same conditions as those laid down for materials used in contact with water intended for human consumption, considering in particular that ion-exchange resins are currently covered by the provisions of the Ministerial Order of 29 May 1997 (as amended).
- the results of migration tests carried out by a laboratory authorised by the Ministry for Health according to two test protocols:
  - o the protocol used for verifying the inertia of the organic materials placed in contact with water intended for human consumption, which has been adapted to the specific characteristics of ion-exchange resins. This protocol is defined in the aforementioned test standards XP P41-250 (Parts 1, 2 and 3) and is supplemented by the measurement of residual levels of DVB and EVB in the resin and the migration water, if these substances appear in the resin's formulation,
  - o the protocol used for testing the elution profile of the TOC, under semi-dynamic conditions as defined by the T 90-601<sup>k</sup> standard.

These migration tests are carried out under the conditions of use recommended by the ion exchanger manufacturer and are designed mainly to assess:

- possible interactions between the resin and the water to be treated, and between the resin and the regeneration products and/or disinfectants employed when using the resin;
- the suitability of the rinsing procedures employed to remove all the solutions used.

The tests are conducted in static conditions that are not representative of the conditions in which ion exchangers are used, which are always dynamic. Moreover, the quantities of resin used for the tests are adapted empirically depending on the tests, and the exchange surface area varies depending on the size of the resin beads.

## **2.2.2 Conditions for renewal of approval**

Under the guidelines established by the CSHPF for applications to renew approval of an ion-exchange resin, and if there has been no change relative to:

- the resin's composition,
- the recommended regeneration and/or disinfectant products,
- the rinsing procedures,

since the date on which approval was obtained, a simplified procedure is applied for renewing approval after five years. Only the following tests are conducted by a laboratory authorised by the Ministry for Health:

- elution profile of the TOC,
- measurement of residual levels of DVB and EVB in the resin and the migration water, if these substances appear in the resin's formulation.

In the event of a modification to the composition of the resin, or the regeneration or rinsing products, the procedure must be repeated in full.

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<sup>j</sup> Circular DGS/SD7A/2003/633 of 30 December 2003 relating to the application of Articles R. 1321-1 *et seq.* of the Public Health Code concerning water intended for human consumption, excluding natural mineral water

<sup>k</sup> Standard T 90-601 of December 1988: Water treatment – Ion-exchange resins – Rerelease test of total organic carbon

### **2.2.3 Call for updating the assessment of ion exchangers prior to marketing**

The procedure used is no longer suited to the current context and needs to be updated in the light of experience gained since the 1980s and the following elements:

- the test protocol for resins currently used by the laboratories authorised by the Ministry for Health to verify the health compliance of the resins is not the one taken into account by the aforementioned European standard NF-EN 12873-3 in force;
- the parameters currently monitored during migration tests (measured in the test water) include some which are no longer relevant, or whose interpretation needs to be reviewed.

The purpose of this document is to identify the scientific evidence necessary for verifying the safety and efficacy of ion exchangers.

On this basis, the laboratories authorised by the Ministry for Health will be able to rule on applications for approval of ion exchangers.

However, files compiled for the assessment of inorganic ion-exchangers such as zeolites, and for innovative ion exchangers, particularly those based on nanoparticles or using nanotechnologies, will continue to be assessed on a case-by-case basis by AFSSA in line with the procedure described in this report.

The laboratories authorised to conduct tests and rule on applications for the approval of ion-exchange resins used for the production of water intended for human consumption must meet the requirements of the Ministerial Order of 18 August 2009 relating to the conditions for authorising laboratories in application of Article R.\* 1321-52 of the CSP.

## 3 Assessment of the safety of ion exchangers

The assessment of the safety of an ion exchanger should be based upon:

- an examination of the compliance of its formulation,
- migration tests carried out on the ion exchanger,
- a comparison of the results of these tests with the criteria of acceptability.

### 3.1 Examination of the chemical formulation

The applicant should send the laboratory authorised by the Ministry for Health in charge of the assessment of the ion exchanger's safety a detailed list of all the chemicals used in the manufacture of the exchanger, and should in particular specify the weight percent of each substance as indicated in Annex C (CAS no., purity, etc.).

These declared substances are compared with:

- the positive lists given in Annex IV of the aforementioned Ministerial Order of 29 May 1997 (as amended),
- the positive lists given in AFSSA's report and opinion of 14 September 2007<sup>l</sup>.

Moreover, if the list contains the substances DVB and EVB, the laboratory must verify compliance with the maximum amounts of these substances, in accordance with the limits defined in the Ministerial Order of 19 October 2006<sup>m</sup>.

The working group proposes revising the examination of the formulation to allow migration tests to be conducted in the case of substances which are known, but which do not appear on the positive lists, and which represent less than 1% of the dry mass of the resin (finished product).

#### 3.1.1 Cases leading to refusal

Examination of the chemical formulation of the ion exchanger will lead to refusal if:

- any of the substances used in the formulation of the ion exchanger do not appear on the aforementioned positive lists and if any of these unlisted substances exceeds 1% of the dry mass of the resin (finished product),
- any of the declared substances appear on the aforementioned positive lists but exceed the corresponding restrictions and/or specifications (adapted for water), for example, for DVB and EVB.

**In these cases the migration tests cannot be performed and the exchanger cannot be marketed for the treatment of water intended for human consumption.**

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<sup>l</sup> Opinion no. 2006-SA-0291 and Report of 14 September 2007 on the positive lists of substances used in the composition of materials in contact with water intended for human consumption

<sup>m</sup> Ministerial Order of 19 October 2006, amending the Ministerial Order of 2 January 2003, on plastic materials and objects in contact with or intended to be in contact with food, food products and beverages.

### 3.1.2 Cases leading to a continuation of the assessment

**The safety assessment continues and the migration tests can be carried out in two situations.** An examination of the formulation is carried out every five years at most when renewing approval of an ion exchanger.

**Situation 1: The examination of the ion exchanger's chemical formulation deems that the ion exchanger's chemical formulation is compliant:**

- all declared substances appear on the aforementioned positive lists and comply with the corresponding restrictions and/or specifications (adapted for water),
- where necessary (for resins made from DVB), the restrictions and/or specifications (adapted for water) for DVB and EVB have been complied with.

**Situation 2: The examination of the ion exchanger's chemical formulation reveals one or more declared substances that do not appear on the aforementioned positive lists:**

- The non-listed substances do not individually exceed 1% of the dry mass of the resin (finished product). This corresponds to a level of impurity which is generally accepted in raw materials commonly used for the manufacture of this kind of product,
- If the concentration of the substance is between 0.1 and 1% of the dry mass of the resin (finished product), it must undergo specific monitoring during the migration tests. It will be screened for in each of the four collections stipulated in the protocol recommended in Section 3.2.2 of this report.

Furthermore, in Situation 2, the manufacturer is recommended to:

- begin the process to register any incriminated substance on one of the aforementioned positive lists,
- or, as far as possible, replace any incriminated substance with substances appearing on the positive lists.

## 3.2 Inertia tests

The inertia tests are designed to assess any possible degradation in quality of the water in contact with the ion exchanger.

### 3.2.1 The existing protocol

The inertia tests conducted on exchangers since 1985 are derived from the protocol described in the aforementioned Circular of 23 July 1985. They are based on the migration tests carried out on organic materials coming into contact with water intended for human consumption defined in the AFNOR experimental standard XP P41-250 (parts 1, 2 and 3) and adapted for ion exchangers as follows:

- Pre-treatment before use is carried out according to the applicant's recommendations (this usually involves percolation with demineralised water or regeneration of the resin);
- The tests are performed under static conditions using 5 cm<sup>3</sup> of resin per litre of water (for measuring the organoleptic parameters and the chlorine consumption) and 50 cm<sup>3</sup> of resin per litre of water for measuring the other parameters;
- The disinfection stage stipulated by the XP P41-250 standard at 50 mg L<sup>-1</sup> of chlorine is carried out in a column using the disinfectant and protocol recommended by the manufacturer. In general, the disinfectant used is peracetic acid or sodium hypochlorite rather than chlorine.

Thus the current protocol includes:

- a rapid screening assay (XP P41-250-1 standard),
- a detailed screening assay (XP P41-250-2 standard),
- a cytotoxicity assay (XP P41-250-3 standard),
- if necessary, an assessment of the restrictions and/or specifications for EVB and DVB,

- a TOC profile (T 90-601 standard).

- **Rapid screening assay**

Carried out according to the XP P41-250-1 standard, this mainly serves to assess the exchanger's influence on the water's organoleptic quality. Certain key or general chemical parameters, such as the exchanger's consumption of chlorine and the total organic carbon leached by the exchanger, are also measured.

In accordance with the requirements of Circular 99 / 217 of 12 April 1999, the results of the rapid screening assays (according to XP P41 250-1) must demonstrate:

- that there is no increase in taste at a threshold greater than 2, after four immersions, or after seven immersions, and that a steady decrease in the taste threshold is observed;
- that there is no increase in  $\text{KMnO}_4$  oxidisability in an acid medium greater than or equal to 1 (mg/L  $\text{O}_2$ ),
- that the increase in chlorine consumption does not exceed 25%,
- that the increase in  $\text{NH}_4$ ,  $\text{NO}_2$  and TOC concentrations is not greater than 0.1 mg/L  $\text{NH}_4$ , 0.02 mg/L  $\text{NO}_2$  and 0.1 mg/L C respectively.

- **Detailed screening assay**

Carried out according to the XP P41-250-2 standard, this serves to assess any possible migration into the water of mineral and organic micropollutants, toxic or undesirable, such as for example polycyclic aromatic hydrocarbons, certain haloforms and metals. It also includes an analysis by gas chromatography coupled with mass spectrometry (GC/MS) for detecting the potential migration of molecules from by-products of polymerization or impurities existing in the basic constituents.

In accordance with the requirements of Circular 99 / 217 of 12 April 1999, the results of the detailed screening assays must comply with the maximum increases given in Table III below.

- **Cytotoxicity assay**

Carried out according to the XP P41-250-3 standard, this provides information on the overall toxicity that may be induced by the resin, due to the presence of any substances not detected by chemical analysis.

In accordance with the requirements of Circular 99 / 217 of 12 April 1999, the results of the cytotoxicity assay are considered satisfactory when the percentage of RNA synthesis compared to the control is greater than or equal to 70%.

- **Assessment of compliance with the restrictions and/or specifications for divinylbenzene (DVB) and ethylvinylbenzene (EVB)**

Measurements of residual levels of DVB and EVB in resin and migration water are carried out if these substances were included in the chemical composition of the resin. The maximum tolerated concentrations of DVB and EVB were defined in the aforementioned Ministerial Order of 19 October 2006.

**Table III: Criteria of acceptability for the materials assessed according to the XP P41-250 standard**

| Parameters                                 | Criteria of acceptability (increase with respect to the control)                                         |
|--------------------------------------------|----------------------------------------------------------------------------------------------------------|
| <u>Physico-chemical parameters:</u>        |                                                                                                          |
| TOC                                        | 1 mg/L                                                                                                   |
| <u>Mineral micropollutants:</u>            |                                                                                                          |
| Mercury                                    | 0.2 µg/L                                                                                                 |
| Cadmium                                    | 1 µg/L                                                                                                   |
| Selenium                                   | 2 µg/L                                                                                                   |
| Antimony                                   | 2 µg/L                                                                                                   |
| Chrome                                     | 10 µg/L                                                                                                  |
| Arsenic                                    | 2 µg/L                                                                                                   |
| Lead                                       | 2 µg/L                                                                                                   |
| Nickel                                     | 4 µg/L                                                                                                   |
| <u>Organic micropollutants:</u>            |                                                                                                          |
| Polychlorinated biphenyls (PCBs)           | 0.1 µg/L                                                                                                 |
| Polycyclic Aromatic Hydrocarbons (PAHs)    | 0.2 µg/L for all 6 substances *                                                                          |
| Halogenated volatile organic compounds     | 3 µg/L for carbon tetrachloride<br>2 µg/L for tri- and tetrachloroethylene<br>20 µg/L for all the THMs** |
| Non-halogenated volatile organic compounds | 1 µg/L for each compound detected                                                                        |
| GC/MS profile                              | 1 µg/L for each compound detected                                                                        |

\* fluoranthene, benzo(3,4)fluoranthene, benzo(11,12)fluoranthene, benzo(3,4)pyrene, benzo(1,12)perylene, indeno(1,2,3-cd)pyrene

\*\* chloroform, bromoform, dibromochloromethane and dichlorobromomethane

#### - TOC profile

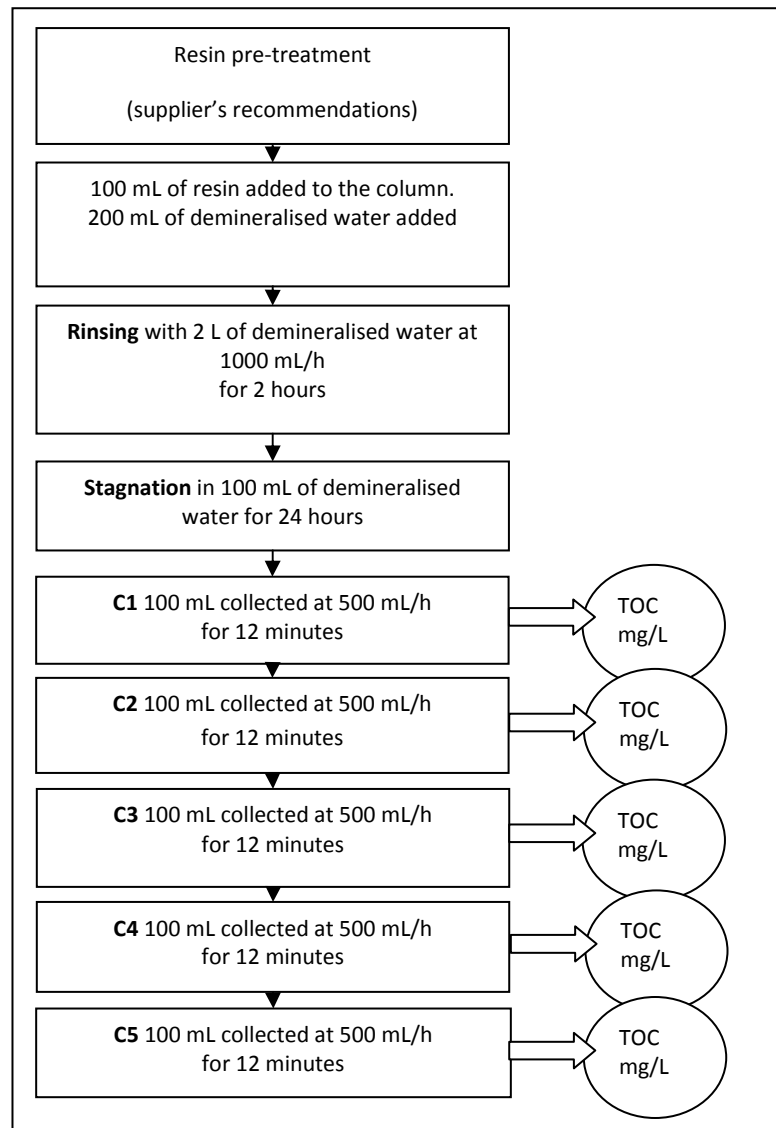
Under the system in place since 1985, a test of the TOC elution profile (under semi-dynamic conditions) is also conducted according to the AFNOR T 90-601 standard of December 1988. According to this standard, which is also used by industry to assess its production, the resin undergoes stagnation for 24 hours in demineralised water before a collection is made of five successive 100 mL portions of demineralised water having percolated through 100 mL of resin at a rate of 500 mL/h.

- The testing device (without a sample) is verified before the test and the level of TOC on output from the column must be less than 0.5 mg/L.
- The demineralised water used is verified and its TOC content ( $C_b$ ) must also be less than 0.5 mg/L.
- The TOC is analysed using the five portions, and the sum of the TOC values from the five collections must not exceed **10 mg/L** (criteria of acceptability):

$$\sum_{n=1}^5 (C_n) - 5 C_b < 10 \text{ mg/L}$$

where  $C_n$  = TOC test n

**Figure 1: Block diagram showing implementation of the T 90-601 standard**



- **Requirements for the sample analysed**

The exchanger sample upon which the inertia tests are carried out must meet the following criteria:

- the chemical composition used for industrial production is identical to that used for producing the resin sample concerned by the authorisation application;
- the manufacturing conditions of the sample submitted for testing are representative of the resin's conditions of production and use.
- if an exchanger offers a variety of resin bead sizes, for the same chemical composition and formulation, the tests are conducted on the exchanger with the smallest bead size since it will have the greatest exchange surface area.

### 3.2.2 Proposed protocol to apply to samples of ion-exchange resins for assessing their safety

The XP P41-250 standard is poorly suited to treatment media such as ion exchangers which need to be tested under dynamic or semi-dynamic conditions. The EN 12873-3 standard of June 2006 applies a semi-dynamic protocol which corresponds to the actual conditions of use of ion exchangers. To conform with the European context regarding trade in goods and to facilitate recognition of assessments between member states, the proposed protocol adopts the entire European protocol for obtaining migration samples. However, this protocol has been expanded, in order to retain the relevant tests conducted since 1985. The proposed protocol therefore involves several tests:

- generation of a TOC elution profile in accordance with the T 90-601 standard, carried out according to the methods and based on the criteria of acceptability set by the French protocol applied since 1985. This profile must be obtained before the protocol adapted from the EN 12873-3 standard can be applied, and if the TOC values are higher than the standard's criteria of acceptability **the marketing of the exchanger must not be authorised**.
- conduct of a semi-dynamic test adapted from the aforementioned EN 12873-3 standard.

The requirements concerning the analysed exchanger sample are maintained.

#### 3.2.2.1 Tests not adopted

The tests carried out according to the XP P41-250 1, 2 and 3 standards have been replaced by tests from the EN 12873-3 standard. This standard is specific to ion exchangers and is more suitable than the materials standards used previously. Accordingly, certain tests whose results needed expert interpretation, particularly the tests in chlorinated water and the cytotoxicity tests, have been abandoned in favour of tests which are more easily interpreted in the case of ion exchangers.

With regard to assessing compliance with the restrictions and/or specifications as specified in AFSSA's opinion of 19 April 2002<sup>n</sup>, the analyses relating to the presence of DVB and EVB in ion-exchange resins are not able to verify their absence in the water in contact with the resin. Therefore, the assessment of the maximum quantity of divinylbenzene (DVB) and ethylvinylbenzene (EVB) in the resin has not been adopted.

#### 3.2.2.2 Description of the semi-dynamic test adapted from the EN 12873-3 standard

This test is conducted in the laboratory according to the steps described in the diagram in Figure 2, on exchanger samples provided by the applicant. The test also includes a control, i.e. a test of an identical system which does not include a resin sample, carried out according to the steps described in the diagram in Figure 3.

The columns used for testing, with a capacity of 1000 mL or 2000 mL, must correspond to the EN 12873-3 standard (Annex B) which mainly states that the system used for verifying safety should include:

- a tank with a capacity of 10 L,
- a pump,
- a column 50 mm in diameter and with a minimum height of 400 mm,
- a mark at 500 mL to indicate the fill level for the ion exchanger.

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<sup>n</sup> AFSSA opinion of 19 April 2002 on a report relating to the presence of divinylbenzene (DVB) and ethylvinylbenzene (EVB) in ion-exchange resins (ref 2001-SA-0215)

- **Obtaining samples of migration water**

**Samples of migration water are obtained according to the protocol described in the EN 12873-3 standard.**

However, the European standard makes no provision for carrying out the migration test after the exchangers have been disinfected. Yet this step can sometimes be detrimental to the ion exchangers when it is carried out under unsuitable conditions (concentrations, temperature, etc.). The working group therefore recommends the addition of extra steps in order to verify the absence of migration after the disinfection stage. The aim of steps 10 *et seq.*, indicated in grey in Figure 2, is to verify that the disinfection protocol does not degrade the exchanger too quickly. It must be conducted for each exchanger, according to the manufacturer's recommendations, and may, depending on these recommendations, be combined with the regeneration and rinsing of the exchanger.

**With regard to the application of the protocol, the working group provides the following details:**

The exchanger volume of 500 mL indicated in step 2 of Figure 2 is fixed, regardless of the diameter of exchanger beads used. The "surface area/volume" ratios are greater than in the protocol currently used in France. **When the same ion exchanger is available in several different bead sizes, the smallest bead size (i.e. the one with the greatest exchange surface area) is the one that is tested.**

The ion exchanger is tested with the regenerating agent recommended by the applicant.

The demineralised water used in steps 2 *et seq.* of Figure 2 complies with the requirements of the EN 12873-3 standard, Section 4.1:

- absence of chlorine,
- conductivity at 25°C less than 20 µS/cm,
- TOC less than 0.2 mg/L,

**The exchangers must be tested with all disinfectants recommended by the manufacturer** and, for each disinfectant, the protocol must be repeated in full, as many times as necessary, although only the T4 collection will be analysed.

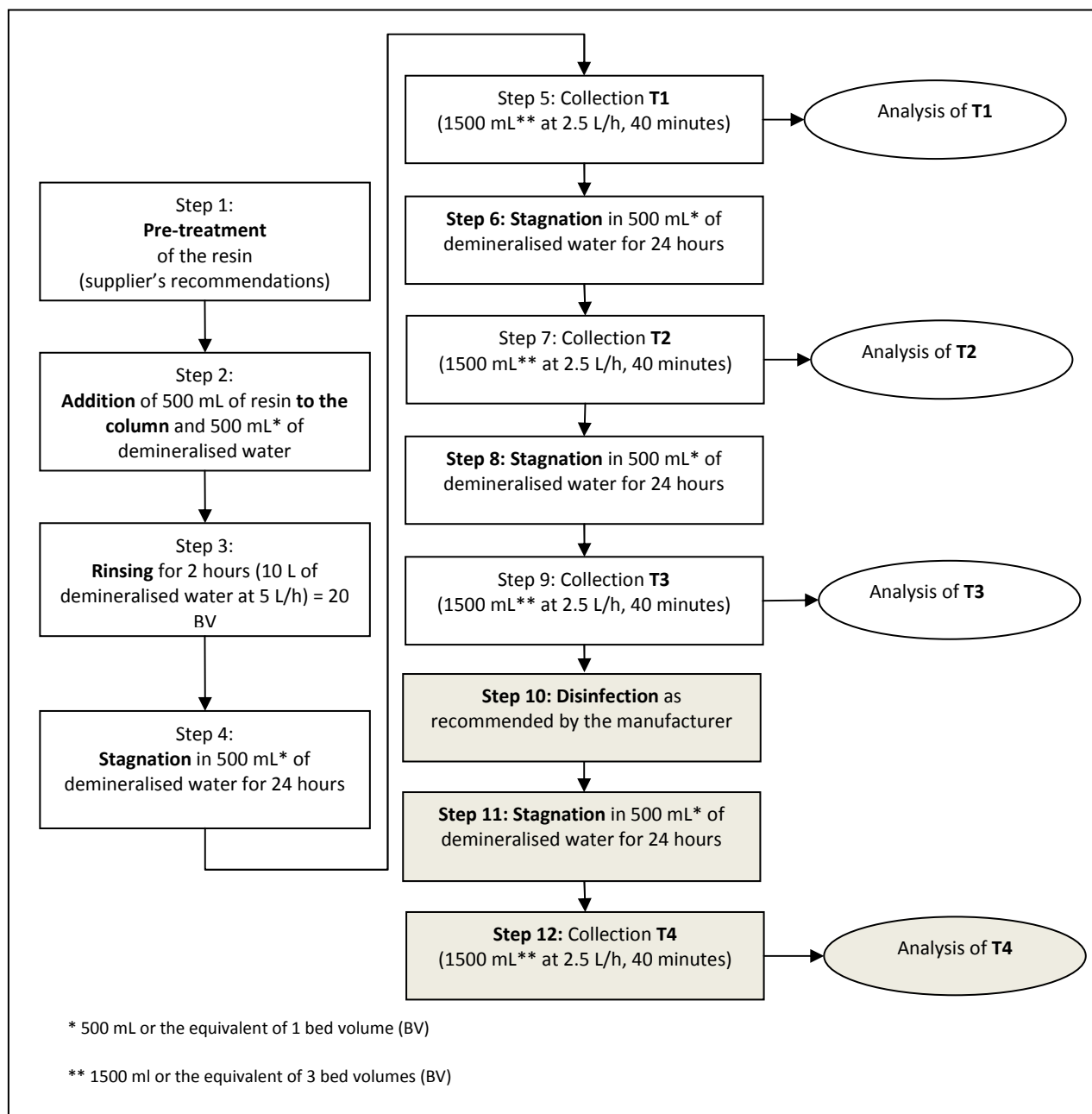
**In the event that different regenerating agents are used, the protocol must be followed in full for each one.**

- **Obtaining samples of control water**

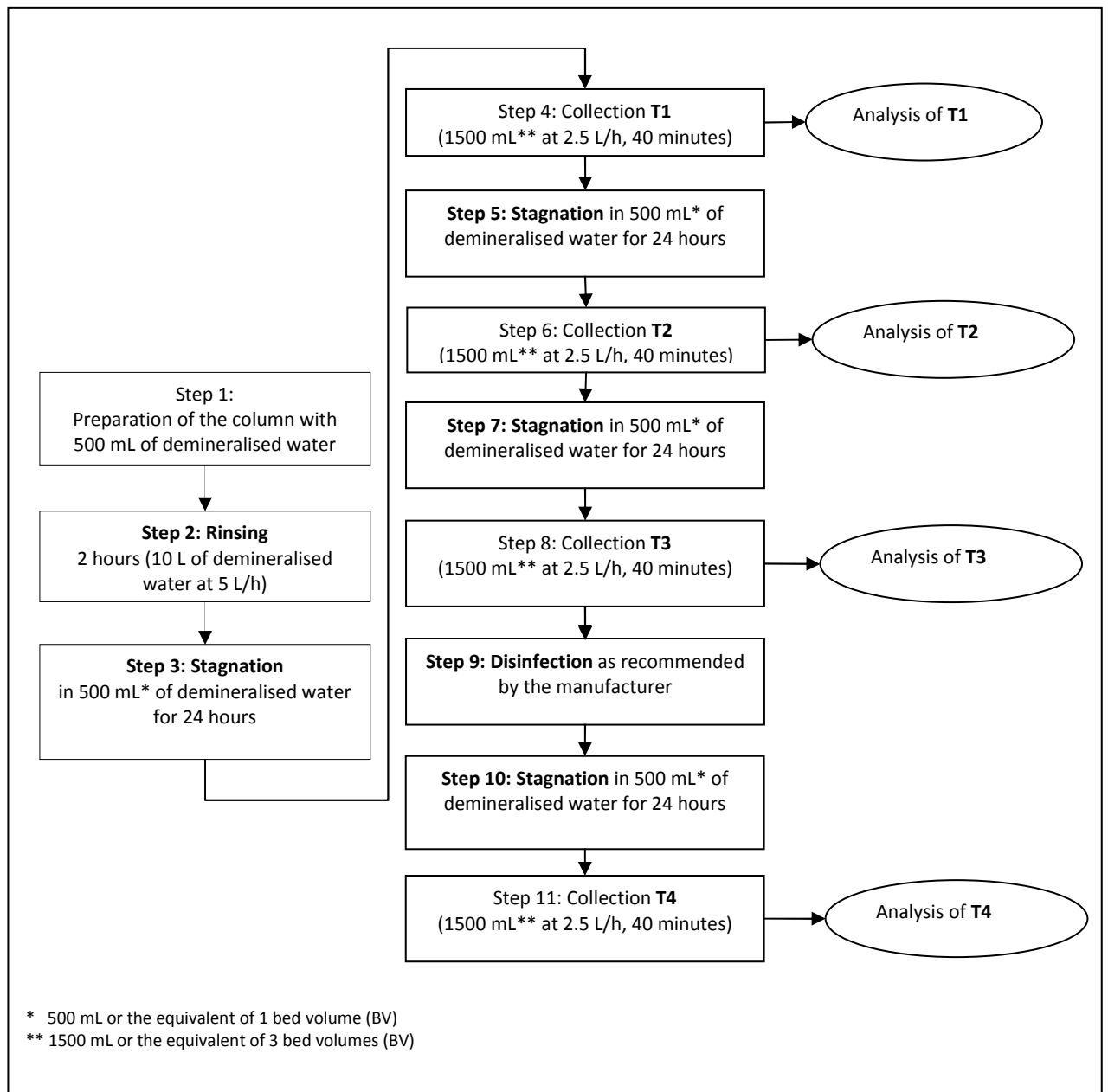
Given the leaching that may result from the test system itself, it is essential to conduct a control test. This test consists in applying the water contact conditions protocol to a system that is identical to the one used to test the ion exchanger, but without any samples. This ensures that no migration associated with the test system interferes with the analysis results, and thus clearly determines the migration due to the ion exchanger.

The protocol for producing the control sample is given in Figure 3. It must be applied at the same time as the test protocol with the resin on a device of identical composition.

**Figure 2: Block diagram showing performance of tests according to the EN 12873-3 standard, supplemented by steps 10 *et seq.***



**Figure 3: Block diagram showing generation of the control sample**



### 3.2.2.3 Parameters and quality criteria for the semi-dynamic test

- **Choice of parameters**

The working group based its proposals on the parameters monitored in the French protocol applied since 1985. It recommends retaining, for the four collections T1, T2, T3 and T4, the analysis of the organoleptic parameters (smell and taste) and the general physico-chemical parameters (TOC and chlorine demand in the elution water). With regard to the minerals, the working group believes that this screening should take place on a case-by-case basis, only for those minerals used in the chemical composition and/or the manufacture of the ion exchanger tested.

With regard to screening for organic micropollutants, the working group wishes to retain the analysis of solvents: halogenated and non-halogenated volatile organic compounds (see the list in Annex D), as well as generation of the GC/MS profile.

It also recommends adding the generation of an LC/MS profile which may be of use in the future, and the analysis of specific compounds used in the resin's composition and/or manufacture (such as chloroacetic acid, NDMA, etc.).

Moreover, the laboratory responsible for applying the protocol will eventually have to monitor any compound(s) not appearing on the positive lists and whose mass concentration is between 0.1 and 1% identified during the examination of the chemical formulation of the ion exchanger (finished product).

- **Establishing criteria of acceptability**

In the protocol applied since 1985, the criteria of acceptability correspond to 20% of the WHO guideline values, or alternatively, the commonly accepted value of 1 µg/L expressed as the closest alkane where screening is carried out. Note that in this specific case, inherited from tests conducted on materials, the volume of test water is 1000 mL for a volume of resin of 50 mL.

For the new protocol, the working group proposes reviewing the process by taking into account the following points:

- the ratio of resin volume/test water volume is greater in the European protocol (1500 mL) than in the one applied since 1985 (1000 mL). At the same time, the volume of resin is 500 mL compared with 50 mL;
- the migration analyses are carried out after the stagnation phases, which correspond to the times when leaching is most likely to occur;
- as the exchanger is used, it regulates itself and leaching of undesirable compounds is reduced;
- no migration test is conducted on the exchanger after use, to monitor the effect on its safety of aging;
- It is not feasible to maintain the criteria applied to materials for the exchangers because:
  - the surface area of the treatment medium in contact with the water is greater than with piping materials,
  - the treatment medium is designed to alter certain characteristics of the water.

The working group therefore proposes applying a safety factor with a value of 2 to the criteria of acceptability applied since 1985.

Therefore, in line with the European protocol, the criteria equivalent to those used since 1985 will be 6/5 of the guideline values and **the working group proposes setting the new criteria at 3/5 of the guideline values applicable to the parameters used for water intended for human consumption. These new criteria offer greater security than those applied since 1985.**

The proposed criteria are therefore 3/5 of the threshold values for substances included in the Ministerial Order of 11 January 2007.

For substances not included in the Ministerial Order of 11 January 2007, the same reasoning can be applied with respect to the guideline values recommended by the WHO (3/5).

For substances not included in the Ministerial Order of 11 January 2007, nor in the WHO recommendations, the proposed criterion of acceptability is 3 µg/L.

The working group emphasised that a concentration of 3 µg/L in migration water would correspond to a substance added at  $7.5 \times 10^{-4}\%$  of the mass of the ion exchanger (assuming that all of the substance migrates), which is well below the limit of 0.1% proposed by the group in the examination of the chemical formulation.

The criteria of acceptability based on cumulative methods represent a good decision support tool, even if these methods do not always identify the molecules. Given both that the databases of mass spectrometers coupled with liquid chromatography are not standardised and must be generated by each laboratory, and that the analytical protocol significantly modifies the method of acquisition and identification, the LC/MS analysis method is only recommended initially as a guide. Considering its advantages and the speed of progress in this analytical field, past experience should be analysed and a technology watch carried out in order to be able to apply these criteria of acceptability to the results of analyses obtained using LC/MS.

**Table IV: Summary of parameters and criteria used**

| Parameters                                                                                                                                       | Criteria                                                                                                                                                                                                             |
|--------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Organoleptic parameters</b>                                                                                                                   |                                                                                                                                                                                                                      |
| Smell and taste                                                                                                                                  | threshold 3                                                                                                                                                                                                          |
| <b>Physico-chemical parameters</b>                                                                                                               |                                                                                                                                                                                                                      |
| TOC                                                                                                                                              | 3 mg/L                                                                                                                                                                                                               |
| Chlorine demand in the elution water                                                                                                             | 40%<br>This value incorporates the background noise estimated at 10% and the accuracy of the method corresponding to 3 times the background noise                                                                    |
| <b>Mineral micropollutants</b>                                                                                                                   |                                                                                                                                                                                                                      |
| To be screened specifically depending on the exchanger's composition (mercury, cadmium, selenium, antimony, chrome, arsenic, lead, nickel, etc.) | 3/5 of the parametric values of the Ministerial Order of 11 January 2007<br><i>or alternatively 3/5 of the WHO's guideline values<br/>or alternatively 3 µg/L</i>                                                    |
| <b>Organic micropollutants</b>                                                                                                                   |                                                                                                                                                                                                                      |
| Volatile organic compounds (halogenated or non-halogenated)                                                                                      | 3/5 of the parametric values of the Ministerial Order of 11 January 2007<br><i>or alternatively 3/5 of the WHO's guideline values<br/>or alternatively 3 µg/L</i>                                                    |
| GC/MS profiles                                                                                                                                   | 3/5 of the parametric values of the Ministerial Order of 11 January 2007<br><i>or alternatively 3/5 of the WHO's standards<br/>or alternatively 3 µg/L per compound<br/>and 20 µg/L in total</i>                     |
| LC/MS profiles                                                                                                                                   | For information                                                                                                                                                                                                      |
| Specific monitoring (such as: EVB, DVB, NDMA, Chloroacetic acid, etc.)                                                                           | 3/5 of the parametric values of the Ministerial Order of 11 January 2007<br><i>or alternatively 3/5 of the WHO's standards<br/>or alternatively 3 µg/L<br/>and Specific Migration Limit (SML)/20 where it exists</i> |
| Specific monitoring of substances representing between 0.1 and 1% of the exchanger's dry mass                                                    | 3 µg/L per compound and 20 µg/L in total                                                                                                                                                                             |

### 3.2.3 Assessment of the safety of inorganic ion exchangers (zeolites, etc.)

**For regulation purposes, inorganic ion exchangers fall within the innovative processes category, which means that their authorisation applications are still assessed by AFSSA on a case-by-case basis.**

These media naturally have very large specific surface areas and contain high concentrations of exchangeable cations (see Annex A, Section 1.3.), mainly  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ .

Commercial zeolites are usually 'doped' with metals, either to increase the specific surface areas and therefore the exchange capacity, or to improve selectivity with respect to certain cations. For example, the clinoptilolite, which in its natural state prefers retaining  $\text{NH}_4^+$  ions through exchange with  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  (Sprynskyy *et al.*, 2005<sup>o</sup>) can, when it is doped with iron (Doula and Dimirkou, 2007<sup>p</sup>), prefer the extraction of copper (from 13.6 mg/g to 37.5 mg/g).

The parameters to be assessed for this kind of ion exchanger must therefore be directly related to the chemical characteristics of these media.

#### 3.2.3.1 Water contact conditions protocol for inorganic ion exchangers

The water contact conditions protocol is the same as for organic exchangers. A control is carried out on the test system without any ion exchanger sample, according to the water contact conditions protocol shown in Figure 3. Setting up the test with the ion exchanger sample is also carried out according to the 2009 water contact conditions protocol shown in Figure 2. The analyses are conducted on all four collections, T1 to T4.

#### 3.2.3.2 Specific parameters for analysis and criteria of acceptability

The parameters for analysis are shown in Table V. They are the same as for organic ion exchangers, supplemented by all the mineral elements used in the exchanger's composition, measured using the GF-AAS, ICP-AES or ICP-MS methods. The other minerals are highly soluble in water and are therefore considered to be eliminated in the rinsing procedure.

The criteria are based on the same considerations as for organic ion exchangers.

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<sup>o</sup> Sprynskyy, M., Lebedynets, M., Terzyk, A. P., Kowalczyk, P., *et al.* (2005) Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *Journal of Colloid and Interface Science*, 284, pp. 408-415.

<sup>p</sup> Doula, M. K. and Dimirkou, A. (2007) Use of an iron-overexchanged clinoptilolite for the removal of  $\text{Cu}^{2+}$  ions from heavily contaminated drinking water samples. *Journal of Hazardous Materials*, 151, pp. 738-745.

**Table V: Summary of parameters and criteria used for inorganic ion exchangers**

| Parameters                                                                  | Criteria                                                                                                                                                                                              |
|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Organoleptic parameters</b>                                              |                                                                                                                                                                                                       |
| Smell and taste                                                             | threshold 3                                                                                                                                                                                           |
| <b>Chemical parameters</b>                                                  |                                                                                                                                                                                                       |
| TOC                                                                         | 3 mg/L                                                                                                                                                                                                |
| Chlorine demand                                                             | 40%                                                                                                                                                                                                   |
| <b>Mineral elements</b>                                                     |                                                                                                                                                                                                       |
| Determination of mineral elements using FAAS or GF-AAS or ICP-AES or ICP-MS | 3/5 of the parametric values of the Ministerial Order of 11 January 2007<br><i>or alternatively 3/5 of the WHO's standards</i><br><i>or alternatively 3 µg/L</i>                                      |
| <b>Organic micropollutants</b>                                              |                                                                                                                                                                                                       |
| Volatile organic compounds (halogenated or non-halogenated)                 | 3/5 of the parametric values of the Ministerial Order of 11 January 2007<br><i>or alternatively 3/5 of the WHO's standards</i><br><i>or alternatively 3 µg/L</i>                                      |
| GC/MS profiles                                                              | 3/5 of the parametric values of the Ministerial Order of 11 January 2007<br><i>or alternatively 3/5 of the WHO's standards</i><br><i>or alternatively 3 µg/L per compound</i><br>and 20 µg/L in total |
| LC/MS profiles                                                              | For information                                                                                                                                                                                       |
| Specific monitoring of substances representing between 0.1 and 1%           | 3 µg/L per compound and 20 µg/L in total                                                                                                                                                              |

### 3.2.4 Assessment of the safety of other ion exchangers (membranes, etc.)

These applications must be sent to AFSSA where they are assessed on a case-by-case basis.

The water contact conditions protocol applied for assessing membrane systems is identical to that typically applied for membranes used for water treatment.

The information contained in the files that are sent must be based on the guidelines established in this report for ion exchangers.

### 3.2.5 Analysis methods

The recommended analysis methods are shown in Table VI.

**Table VI: Recommended analysis methods**

| Parameters                                                                                                                                                     | Analysis method                                                                                                                                                                                                              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Organoleptic parameters</b>                                                                                                                                 |                                                                                                                                                                                                                              |
| Smell and taste                                                                                                                                                | NF EN 1622                                                                                                                                                                                                                   |
| <b>Physico-chemical parameters</b>                                                                                                                             |                                                                                                                                                                                                                              |
| TOC                                                                                                                                                            | NF EN 1484 <sup>q</sup>                                                                                                                                                                                                      |
| Chlorine demand                                                                                                                                                | Method detailed in Annex E                                                                                                                                                                                                   |
| <b>Mineral micropollutants</b>                                                                                                                                 |                                                                                                                                                                                                                              |
| To be screened for on a case-by-case basis depending on the exchanger's composition (e.g. mercury, cadmium, selenium, antimony, chrome, arsenic, lead, nickel) | Reference to the performance characteristics stipulated in Annex II of the Ministerial Order of 17 September 2003 <sup>r</sup>                                                                                               |
| <b>Organic micropollutants</b>                                                                                                                                 |                                                                                                                                                                                                                              |
| Volatile organic compounds (halogenated or non-halogenated)                                                                                                    | See illustrative list in Annex D<br>Static headspace analysis and determination using GC/MS<br>XP P41-250-2 Annex D <sup>s</sup><br>EN ISO 10301 <sup>t</sup><br>NF ISO 11423-1 <sup>u</sup><br>NF EN ISO 15680 <sup>v</sup> |
| GC/MS profiles                                                                                                                                                 | Pr NF EN 15768 <sup>w</sup><br>In the event that a compound is detected with this technique, it is recommended to quantize it using an alkane standard and if possible to identify it                                        |
| LC/MS profiles                                                                                                                                                 | Non-standard method<br>In the event that a compound is detected with this technique, it is recommended to quantize it and if possible to identify it                                                                         |
| Specific monitoring (such as: EVB, DVB, NDMA, Chloroacetic acid, etc.)                                                                                         | Specific methods                                                                                                                                                                                                             |

<sup>q</sup> Standard NF EN 1484 July 1997: Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

<sup>r</sup> Ministerial Order of 17 September 2003 on methods for analysing water samples and their performance characteristics

<sup>s</sup> Standard XP P41-250-2 December 2001: Effects of materials on the quality of water intended for human consumption - Organic materials - Part 2: measurement method for the organic and mineral micropollutants – Annex D: Dynamic headspace technique for determining volatile organic compounds

<sup>t</sup> Standard EN ISO 10301 April 1997: Water quality - Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods

<sup>u</sup> Standard NF ISO 11423-1 September 1997: Water quality - Determination of benzene and some derivatives - Part 1: headspace gas chromatographic method

<sup>v</sup> Standard NF EN ISO 15680 January 2004: Water quality - Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

<sup>w</sup> Pr (Draft) NF EN 15768: The GC-MS identification of water leachable organic substances from materials in contact with water intended for human consumption

### **3.2.6 Procedure for renewing approval or for a change of formulation**

The exchangers are systematically reassessed according to the full procedure after the five-year period.

In the event that the formulation contained any substance not appearing on the positive lists accepted during the earlier approval, the applicant is advised to indicate whether it has undertaken the assessment procedures for these substances, if it has replaced the non-listed substance by another, or if nothing has changed.

Further information must nevertheless be provided if the applicant wishes to:

- use a different regenerating product to those tested when seeking approval, and if this is the case, all the inertia tests should be carried out.
- use a different disinfectant to those tested when seeking approval, and if this is the case, only the analysis on collection T4 will be performed.

In the event that there is any change in the exchanger's chemical composition or manufacture, the applicant must inform the Directorate General for Health and a total reassessment of the exchanger's safety must be carried out. When this new assessment has been completed and if all the tests confirm compliance, approval will again be issued for five years.

The changes may relate to products included in the ion exchanger's formulation or that of the components involved in the manufacturing process (pH correctors, anti-foam, etc.).

The applicants use the terms 'minor change' and 'major change' but the laboratory conducting the tests will not be able to determine whether the changes made by the manufacturer are minor or major. As a result, and pending any feedback, the working group considered that no distinction could be permitted in the modifications imposed on the exchangers, and proposes resuming its work later in analysing the different changes declared by the producers.

## 4 Recommendations for use

### 4.1 General recommendations

The lifetimes of ion-exchange resins vary greatly as they depend on parameters that are difficult to control. In particular they are highly sensitive to temperature and oxidants because the metals in contact with the oxidants may catalyse oxidation. In terms of exchange efficiency, the resins have lifetimes estimated at several years, at temperatures between 0° and 40°C. According to the producers, some resins can resist short-term (1 to 2 hours) thermal shocks of 80°C, but continuous use at 80°C may cause a significant reduction in this lifetime.

When internal distribution systems are disinfected, the very high concentrations of chlorine used can lead to the formation of chlorination by-products, through interaction with the organic matter adsorbed by the resin. It is therefore essential to by-pass the exchangers or remove them from the circuit when disinfecting internal distribution systems.

The recommended storage conditions should be specified for all ion-exchange resins, namely temperature and storage period prior to use. An expiry date for the first use must be indicated on each batch of resin.

Repeated drying and rehydration may cause most of the structures in gel-type resins to break down. They must therefore always be kept moist.

The supplier must specify both the recommendations concerning intermittent use of the resin (particularly for domestic use) and the procedure to be followed in the event that the resin is not used for a prolonged period (regeneration, disinfection, etc.).

Finally, approval is granted for a given use of the resin and for the form in which it will be used, in accordance with the regeneration and disinfection conditions provided by the supplier. **The resin supplier and seller must therefore specify the regenerating agent(s) and disinfectant(s) having obtained approval with the resin for a given use.**

### 4.2 Risks associated with the use of resins, and recommendations

#### 4.2.1 Softening

The strong cation resins in sodium form provide water that is rich in sodium and slightly aggressive. After such treatment, it is a good idea to counteract this aggressivity. Users following a low-sodium diet should be warned.

The implementation conditions may vary depending on their use. Regeneration may be carried out on-site, however the resulting waste will be heavily laden with chloride. Depending on the case, rinsing effectiveness can be controlled either by verifying the water's conductivity, or by simply measuring the volume of water used.

When resins are used in water treatment plants, meters measure the volume of rinsing water. However, in domestic use, this volume is very often estimated by the rinsing time. This measurement method may, if the water pressure in the system falls, lead to under-rinsing and the release in the system of water that is heavily loaded with chlorides and highly corrosive.

#### 4.2.2 Decarbonation

The most commonly used exchangers are weak cation resins in H<sup>+</sup> form. When using resins with –COOH carboxylic functional groups, CO<sub>2</sub> is produced in small amounts making the water corrosive. This phenomenon should also be described in the specification sheets.

### 4.2.3 Nitrate removal

The resins are most often in anionic chloride form. The precautions to be taken and recommendations to be indicated by the supplier relate to the following:

- modification of the calcium carbonate equilibrium;
- the fact that in the first phase of the exchange cycle the bicarbonate ions are exchanged;
- the fact that the nitrate ions are exchanged with chloride ions in resins which are selective for monovalent ions.

The manufacturer should indicate these phenomena in the specification sheets.

**Given the release of amino compounds that occurs when a plant is shut down, domestic use of anion-exchange resins is prohibited.**

**For industrial use and following any shutdown phase exceeding 12 hours, it is essential that the resin is regenerated.**

### 4.2.4 Demineralisation

The exchangers are strong cation resins in  $H^+$  form and strong anion resins in  $OH^-$  form. For more powerful demineralisation, these two exchangers can be supplemented by a mixed-bed system containing strong anion and strong cation resins.

The regenerating solutions are sulphuric acid or hydrochloric acid and soda.

With mixed resins, the resins must be separated before regeneration.

## 4.3 Products that may interfere with the functioning of the resins

Metals including iron, organic acids including humic acids, as well as suspended solids, oils, surfactants and polyelectrolytes, may disrupt the functioning of the ion-exchange resins. These products may act in different ways:

- by blocking the exchange sites (**poisoning**),
- by **oxidation**,
- by **accumulation**,
- by **causing a loss of pressure**.

This may involve both chemical and mechanical disruption. This kind of phenomenon is sometimes observed in food industries which treat water from the public distribution system that has already been treated using ion-exchange resins in a water purification plant.

Moreover, ongoing contact with oxidants such as chlorine can lead to deterioration of the resin through de-cross-linking depending on the conditions of use.

Iron can act as a catalyst when oxidants such as peroxides are present.

Some types of flocculants and surfactants can also damage the resin.

Producers maintain that there are few problems related to **biological growth** and potential development of **biofilms** in the ion-exchange resins. According to the arguments put forward, water intended for human consumption is treated before it reaches the ion-exchange resins and is therefore uncontaminated. This concerns microorganisms eliminated by the treatment channels, however natural flora found in the system will colonise the media. These developments may occur during long shutdown periods. Although not guaranteed, the regeneration phases should help limit the phenomena of bacterial colonisation.

The tests available for monitoring an ion-exchange resin's state of degradation are:

- the humidity test;
- measuring the effectiveness of the resin, which is based on the fact that certain degradations impede the resin's functions;
- poisoning tests with different molecules.

#### **4.4 Information and recommendations to be provided by manufacturers in specifications sheets for users**

Any information which serves to ensure the safety in use and lifetime of the exchanger must be provided in the specifications sheets, including:

1. storage conditions:
  - maximum period without any special measures needed before use;
  - period associated with special measures needed before use;
  - temperature range for storage;
  - etc.
2. resin characteristics:
  - selectivity;
  - intended use, specifying:
    - o form;
    - o regenerating agent(s) to be used;
    - o disinfectant(s) to be used;
3. precautions for use to avoid premature degradation of the resin:
  - temperature range for use;
  - resin's tolerance to products used for occasional disinfection of the distribution system;
  - etc.
4. precautions to be taken in the event of water stagnation in the resin:
  - period of stagnation after which regeneration is required;
  - period of stagnation after which disinfection is required;
  - period of stagnation after which the resin should be changed;
5. the exchanger's impact on water quality (agressivity, corrosivity).

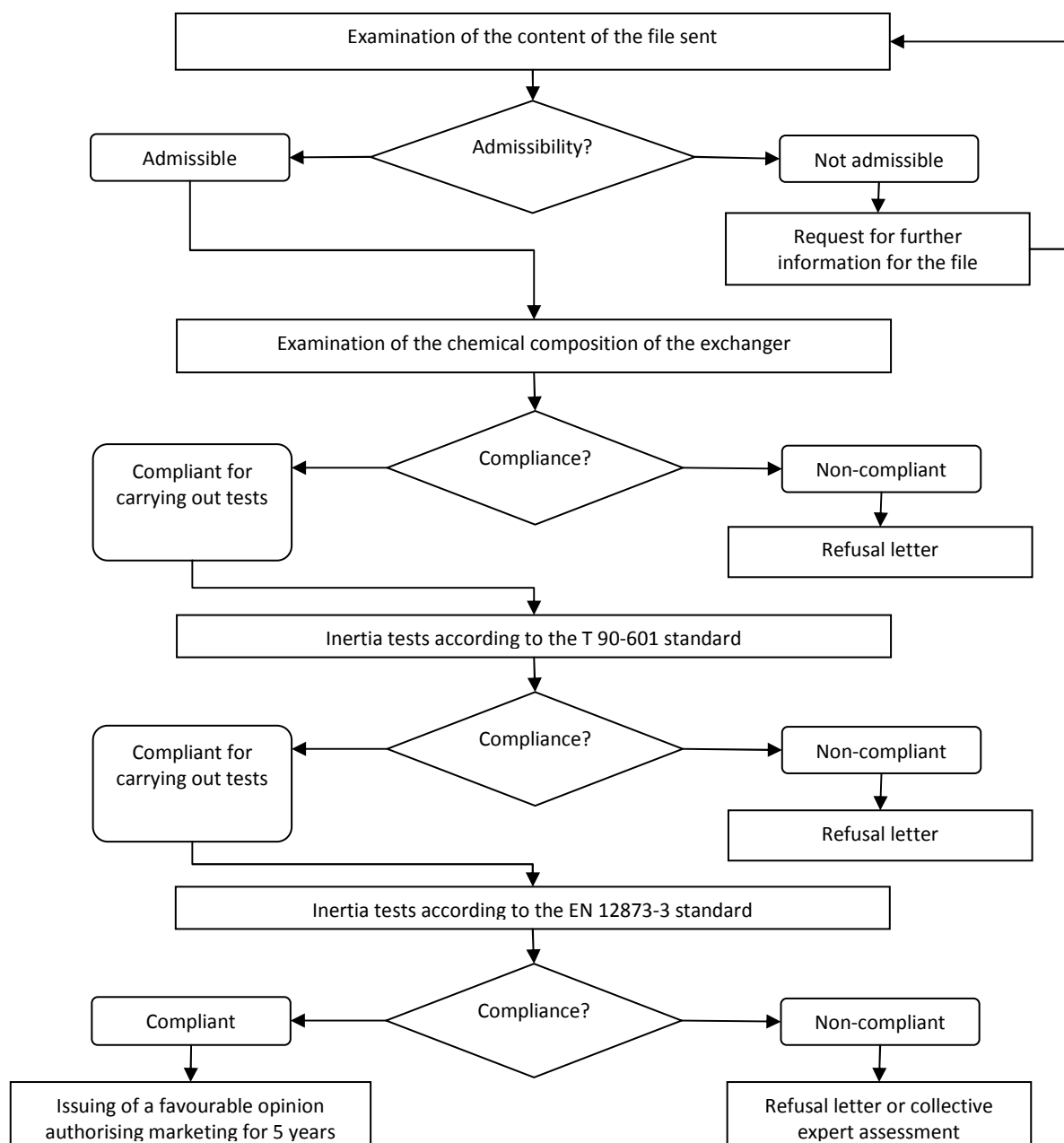
## 5 Guidelines for examining an application to use an ion exchanger

Figure 4 summarises the procedure recommended by the working group for the marketing authorisation for a 5-year period of a process using an ion exchanger for treating water intended for human consumption.

This procedure, based on semi-dynamic tests, is representative of the ion exchangers' conditions of use, and the parameters screened for are adapted to the potential risks and/or migration caused by the exchangers.

Furthermore, this new procedure should reduce the time needed for the assessment of ion exchangers with respect to the procedure applied since 1985.

**Figure 4: Decision tree for assessing the safety of ion exchangers**



The health compliance of the ion exchangers should be verified by a laboratory authorised to this effect by the Ministry for Health. To obtain such authorisation, AFSSA considers that the laboratory:

- should fulfil the obligations defined in the aforementioned Ministerial Order of 18 August 2009 including in particular authorisation for tests of total organic carbon leaching according to the T 90-601 standard;
- must be authorised for carrying out tests and analyses according to the protocol adapted from the EN 12873-3 standard defined in these guidelines, by the French Accreditation Committee (COFRAC) or by any other equivalent European accreditation body that is a signatory to the multilateral agreement entered into as part of the European coordination of accreditation bodies.

The authorised laboratory may issue a favourable opinion according to the standard approval model shown in Annex F if all the steps in the decision tree have been complied with. Where there is a problem of interpretation, particularly if the analysis results are close to the criteria of acceptability when any measurement uncertainty is taken into account, the file may be submitted to AFSSA for review. In addition, the assessment of innovative products and treatment processes remains AFSSA's responsibility (ion exchange membranes, inorganic ion exchangers, products and treatment processes involving nanoparticles, etc.).

AFSSA reiterates that the marketing authorisation for an ion exchanger:

- is issued for a period of 5 years,
- specifies the regenerating agent(s) and the disinfectant(s) tested by the approved laboratory,
- is invalid if any other products are used in contact with the ion exchanger.

## 6 Recommendations

To assess how well the new procedure is being applied and the public's access to the information, as well as to develop the procedure in line with analytical progress, AFSSA recommends that the following six measures be implemented:

- publication, on the website of the Directorate General for Health, of a regularly-updated list of exchangers possessing valid marketing authorisation.
- sending to AFSSA of an annual summary of applications refused by the authorised laboratories, specifying the conditions for the refusal, so as to improve knowledge of the protocol used.
- sending to AFSSA of an annual summary of substances not appearing on the recognised positive lists and included in the formulation of approved ion exchangers.
- generation of an LC/MS profile during the analysis of the 4 collections gathered according to the new water contact conditions protocol. No threshold limit was fixed for this analysis as this method has not been standardised and is not yet used routinely by the authorised laboratories. In addition, the results obtained depend on the protocol and the library available for each analytical system. The working group hopes that in a few years this method will be used routinely by authorised laboratories, as this analytical development will help with the detection of polar compounds that can easily be leached from the resins. AFSSA hopes to receive an annual review of the compounds that the authorised laboratories have detected with this technique, in order to consider, where appropriate, an amendment to the protocol and/or the limits set.
- drafting of specifications sheets for the ion exchangers including imperatively all the information contained in Section 4.
- performance of studies on leaching from exchangers, based on their aging and storage period prior to first use.

In general for all materials, objects, treatment products and processes used in contact with water intended for human consumption, AFSSA recommends:

- that the factory production of each product undergo regular monitoring (audits) by a third party organisation,
- that a plan for obtaining samples for tests be carried out, by a third party organisation, through sampling of products taken at the factory.

## Annex A:

### An overview of ion exchange and its application to water treatment

#### 1. Ion exchange and the main types of ion-exchange resins

##### 1.1. Basic concepts of ion exchange and ion exchangers

Ion exchange on solid material consists in replacing, by exchange, the ions present in a solution with an equivalent amount of ions bound to the resin.

An ion exchanger is an insoluble organic or inorganic material to which the ions to be exchanged can bind. Many natural compounds — such as clay, humic acids, aluminosilicates, zeolites, soils, soil humus/clay-humus complexes, mud and sediments — have ion exchange properties. Synthetic resins are the most widespread ion exchangers used at industrial scales.

Ion exchange reactions are selective and reversible. They can be described using the law of mass action and are characterised by a thermodynamic constant  $K$ , which is the ion exchange or selectivity constant.

Exchange reactions continue until the concentrations of the various ions reach a concentration equilibrium, defined by the equilibrium constant  $K$ . This constant depends on the nature of the exchanged ions, temperature and the concentration for ions of different valence for a given resin.

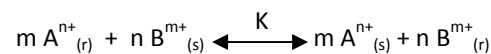
Let

$[A^{n+}]_{(r)}$  = the concentration of ion species A on the resin;

$[B^{m+}]_{(s)}$  = the concentration of ion species B in solution;

$n$  and  $m$  = the charge carried by ion species A and B, respectively ( $n, m = 1, 2$  or  $3$ );

The reaction (I) can be written as:



and the equilibrium constant  $K$  can be written as:

$$K = \frac{[A^{n+}]_{(s)}^m \times [B^{m+}]_{(r)}^n}{[A^{n+}]_{(r)}^m \times [B^{m+}]_{(s)}^n}$$

##### 1.2. Different types of organic ion exchangers and their characteristics

###### 1.2.1. Resin ion exchangers

Synthetic ion-exchange resins are obtained by polymerisation of various monomers (styrene, acrylate, etc.) whose chains can be linked to one another using a cross-linker such as, for example, divinylbenzene in polystyrene resins, and on which functional groups, such as sulfonic or carboxylic acids and quaternary ammonium cations, can be grafted.

Cross-linking forms the backbone of the resin and the mechanical resistance of the resulting material varies with the degree of cross-linking. Cross-linking also modifies the kinetics of exchange and selectivity. It must be calculated so as to obtain mechanical and chemical stability of the resin and still maintain the expected ion exchange properties. The cross-linked polymer is inert and occurs in the form of spherical particles (beads). According to their structure, resins can be classified as

- gel resins (mean porosity, 4 nm);
- macroporous resins (mean porosity, 130 nm).

**Table A1: Different resin polymers and qualities**

| Type of backbone | Type of resin                                  | Particular features                                                                                                        |
|------------------|------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| Polystyrene      | Gel (the oldest and most frequently used type) | High exchange capacity                                                                                                     |
|                  | Macroporous                                    | Weaker exchange capacity than gels,<br>Long life span,<br>Can bind large molecules,<br>Higher exchange kinetics than gels. |
| Polyacrylate     | Gel<br>Macroporous                             | High resistance to poisoning by organic molecules,<br>Excellent mechanical stability.                                      |

The resin can be activated by introducing various functional groups, and the ions that can be exchanged on the resin depend on these functional groups. Thus, for a given resin backbone, cation exchangers or anion exchangers can be obtained.

For **strong acid resins** (sulfonic acid resins), only electrostatic bonds are involved and bond distances are indeterminate. Bound ions can thus have more than one charge (e.g. calcium ions have 2 charges).

However, for **weak acid resins**, which act through covalent bonds, the bond distance is fixed, one ion cannot bind to two charges simultaneously for reasons of steric hindrance. In the case of calcium, the stoichiometry is 1:1. For water with high concentrations of calcium bicarbonate, it is  $\text{Ca}(\text{CO}_3\text{H})^+$  that is bound. The water is thus not only decarbonated but also softened.

On anion exchangers, anionic metal complexes ( $\text{FeCl}_6^{3-}$ ,  $\text{CdCl}_4^{2-}$ ) can bind with distribution coefficients that can be higher than those obtained with complexing resins. In this case, binding curves are bell-shaped, with maximum binding occurring at an optimal chlorine concentration that corresponds to the high stability of the non-charged complex. Above or below this optimal concentration, the complexes do not bind to the resin. Furthermore, separation by gradual elution can be carried out by varying the concentration of, for example, hydrochloric acid to extract the cations one by one from the resin, depending on the stability of their complexes. By using reactions in solution, this type of resin is often more efficient for binding metal cations than complexing resins. Cyanide is specifically used for electroforming. Arseniates can also be eliminated on complexing resins in the iron form.

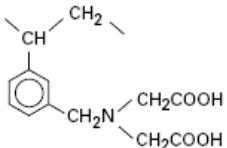
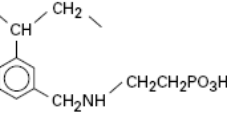
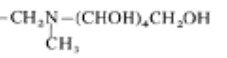
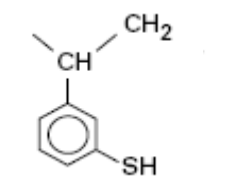
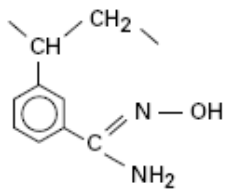
**Table All: Functional groups used on resin ion-exchangers**

| Type of resin                                                                                                             | Functional group (ion exchanger)                             | Use (and indicative working pH range)                                                                                                                                                                                                     | Exchange capacity (Eq.L <sup>-1</sup> resin) |              | Regenerating agents                                                                                             | Selectivity                           |
|---------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------|--------------|-----------------------------------------------------------------------------------------------------------------|---------------------------------------|
|                                                                                                                           |                                                              |                                                                                                                                                                                                                                           | Gel                                          | Macro-porous |                                                                                                                 |                                       |
| <b>Strong acid cation</b><br>SAC (strong cations):<br>$H^+ \ll M^{n+}$<br>$H^+$ ions do not bind as well as other cations | Sulfonic:<br>$-SO_3^-(H)$                                    | Softening<br>(1 – 13)                                                                                                                                                                                                                     | 1.4 to 2.2 g                                 | 1.7 to 1.9   | Strong acid: 2 to 3 times the stoichiometric quantity (HCl or $H_2SO_4$ ) or chloride brine                     | All cations                           |
| <b>Weak acid cation</b> WAC<br>(weak cations):<br>$H^+ \gg M^{n+}$<br>$H^+$ ions bind better than other cations           | Carboxylic:<br>$-COO^-(H)$                                   | Decarbonation:<br>Binds carbonate scale<br>Eliminates heavy metals<br>(4 – 13)                                                                                                                                                            | 3.5 to 4.2                                   | 2.7 to 4.8   | Weak acid: no excess (HCl $H_2CO_3$ or $H_2SO_4$ )                                                              | Preference for polyvalent cations     |
| <b>Strong base anion</b> SBA<br>(strong anions):<br>$OH^- \ll A^{m-}$<br>$OH^-$ ions do not bind as well as other anions  | Quaternary ammonium<br>Type 1:<br>$-N(CH_3)_3^+$             | Total demineralisation:<br>all anions and $CO_2$ are bound when the resin is used in a hydroxide cycle (1 – 12)<br><br>Deacidification, deanionisation, adsorption of organic acids, elimination of specific anions (nitrates, arsenates) | 1.2 to 1.4                                   | 1.0 to 1.1   | Strong base: 2 to 3 times the stoichiometric quantity (sodium hydroxide or chloride brine)                      | All anions from weak and strong acids |
|                                                                                                                           | Quaternary ammonium<br>Type 2:<br>$(C_2H_4OH)-N^+-I(CH_3)_2$ | Complete demineralisation:<br>(1 – 12)<br>Better exchange capacity than Type 1, but weaker chemical resistance                                                                                                                            | 1.3 to 1.5                                   | 1.1 to 1.2   |                                                                                                                 |                                       |
| <b>Weak base anion</b> WBA<br>(weak anions):<br>$OH^- \gg A^{m-}$<br>$OH^-$ ions bind better than other anions            | $-N^+-(CH_3)_2I(OH)$                                         | According to the bound amine group<br>3 types of resin<br>-primary,<br>-secondary<br>-or tertiary<br>(1 – 4)                                                                                                                              | 1.4 to 2                                     | 1.2 to 1.5   | Weak Base: 1 to 1.5 times the stoichiometric quantity (sodium hydroxide, ammonia hydroxide, ammonium carbonate) | Preference for anions of strong acids |

### 1.2.2. Complexing/chelating resins

These resins have specific functional groups that may be naturally present but are usually introduced using chemical methods and form complexes or chelates with metal ions. The functional groups are donors of electron doublets and are associated with atoms such as N, S, O or P and act as classic complexing or chelating agents.

**Table AIII: Most common chelating resins**

| Type of resin                                            | Active functional group on the exchanger                                           | Regenerating agents                                                                | Use (pH range)            | Exchange capacity (en Eq.L <sup>-1</sup> resin) | Selectivity                                                          |
|----------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|---------------------------|-------------------------------------------------|----------------------------------------------------------------------|
| Iminodiacetic chelating                                  |   | HCl (2.5M),<br>HNO <sub>3</sub> (2.5 M),<br>ou H <sub>2</sub> SO <sub>4</sub> (2M) | 1.5 - 9                   | 1.3 – 1.6                                       | High degree of selectivity for heavy metals (and radionuclides)      |
| Aminophosphonic                                          |   | HCl (1M - 2M)                                                                      | 1-10 (depending on metal) | 1 – 1.5                                         | High degree of selectivity for transition metals (and radionuclides) |
| Polyosides (e.g. N-methyl-D-glucamine, bis-picolylamine) |   | Strong acid                                                                        | 0-7                       | 0.8                                             | Borate                                                               |
| Thiol (or mercaptan)                                     |   | HCl 1.5M (divalent metals) to 11 M (mercury)                                       | 1 - 13                    | 1 – 1.4                                         | Divalent metals, including mercury                                   |
| Amidoxime                                                |  | Strong acid                                                                        | 0 - 13                    | 0.8 – 1.9                                       | High degree of selectivity for heavy metals                          |

### 1.3. Different types of inorganic ion exchangers and their characteristics

Although they have been used longer than organic ion-exchange resins, inorganic ion exchangers are still, from a regulatory point of view, considered "innovative" procedures and applications for this type of resin will be examined on a case-by-case basis by AFSSA. Inorganic ion exchangers currently used for water treatment are primarily zeolites.

#### 1.3.1. Physico-chemical characteristics of zeolites

Zeolites are hydrated crystalline aluminosilicates that have been widely used for many years in the chemical industry:

- as catalysts for petrochemistry;
- for purifying gases by adsorption;
- for purifying water containing radioactive metals by specific ion exchange;
- for softening water;
- for eliminating metal cations and organic molecules,
- as adsorbents.

Zeolites are used for their specific physical and chemical properties:

- High crystallinity;
- High thermostability;
- cage structure (interconnections with tunnels and cages) that arises from three-dimensional networks of tetrahedra which link aluminium oxide complexes [AlO<sub>4</sub>]<sup>5-</sup> with silicon oxides [SiO<sub>4</sub>]<sup>4-</sup> that thereby share oxygen atoms (Figure 1); this structure confers high selectivity to zeolites.

Zeolites have the following general formula:  $M_{x/n}^{n+} [Al_x Si_y O_{2(x+y)}]^{x-}, z H_2O$  where M is the exchangeable cation (alkaline, alkaline-earth or transition metal), an ammonium ion, or a proton. According to the value of the y/x ratio, zeolite structures can be classified into several types.

The cation M is responsible for the acid-base properties and the cation exchange properties of zeolites. Zeolites have a large specific surface and contain high concentrations of exchangeable cations (primarily  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ), as well as lithium, barium, strontium and caesium. The exchange capacity can reach 5 mEq/g.

There are more than 180 types of basic structures for natural zeolites (International Zeolite Association (IZA)). The most commonly used are part of the clinoptilolite and chabazite (or acadialite) families [ $Ca_2(Al_4Si_8)O_{24}, 12 H_2O$ ].

**Table AIV: Mean chemical composition of two natural zeolites**

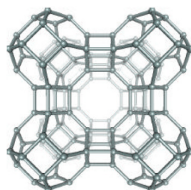
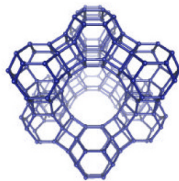
|                                      | Chemical composition (% weight) of the main natural zeolites |           |
|--------------------------------------|--------------------------------------------------------------|-----------|
|                                      | Clinoptilolite                                               | Chabazite |
| SiO <sub>2</sub>                     | 63-72                                                        | 50 - 62   |
| Al <sub>2</sub> O <sub>3</sub>       | 13                                                           | 17        |
| Fe <sub>2</sub> O <sub>3</sub>       | 1.5                                                          | 3.5       |
| CaO                                  | 2.1                                                          | 8.6       |
| MgO                                  | 1.1                                                          | 0.9       |
| Na <sub>2</sub> O                    | 2.1                                                          | 0.5 - 1.5 |
| K <sub>2</sub> O                     | 2                                                            | 1 - 5     |
| MnO                                  | 0.01 - 0.1                                                   | < 0.01    |
| P <sub>2</sub> O <sub>5</sub>        | 0.05                                                         | 0.1 - 0.3 |
| S                                    | 0.03                                                         | < 0.01    |
| Specific surface (m <sup>2</sup> /g) | 28-32                                                        | 60 - 150  |
| CEC (mEq/g)                          | 1-4                                                          | 2.7 – 3.9 |

### 1.3.2. Zeolite nomenclature

The main zeolites used for separation purposes are types A, X and Y. However, there are also type B, L and N zeolites, as well as commercial zeolites of type ZSM and SSZ, neither of whose names comply with the recommendations laid down by the International Union of Pure and Applied Chemistry (IUPAC) and the IZA. IZA has catalogued the 180 structures that have been inventoried to date according to a three-letter code (Framework Type Code), that can be found on the IZA web site (<http://izasc.ethz.ch/fmi/xsl/IZA-SC/ft.xsl>).

Zeolites are classified into types according to their crystalline structure and the Si/Al ratio. The overall charge indicates the number of compensating monovalent cations that the zeolite can accept within its structure (at the scale of the crystalline lattice).

**Table AV: Main types of zeolites**

| Zeolite | Crystal structure                                                                                    | Overall charge | Si/Al    |
|---------|------------------------------------------------------------------------------------------------------|----------------|----------|
| Type A  | Cubo-octahedron<br> | -12            | 1        |
| Type X  | Tetrahedron<br>     | -6 to -12      | 1 to 1.5 |
| Type Y  | Tetrahedron                                                                                          | -6 to -12      | 1.5 to 3 |

For a type A zeolite, the Si/Al ratio is close to 1. Thus, the overall charge of the cube is -12 and it can accept up to 12 monovalent compensating cations. The position of these cations depends on the ion species, but sites are in general positioned near access windows, thereby reducing pore size. A non-compensated type A zeolite with a pore size of 11.4 Å will be reduced to 4 Å if the compensating ion is sodium (called zeolite 4A), to 3 Å if the compensating cation is potassium (zeolite 3A) and to 5 Å if the compensating cation is calcium (zeolite 5A).

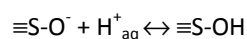
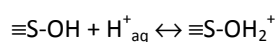
Pore sizes are the greatest in type A zeolites, offering greater possibilities for adsorption of larger molecules.

The difference between types X and Y lies in their Si/Al ratios. This ratio is 1 to 1.5 for type X zeolites and 1.5 to 3 for type Y. This ratio which directly influences the position, and the number of compensating cations, can vary from 6 to 12 according to the type of crystal.

### 1.3.3. Mechanism of ion exchange

When using zeolites, ion exchange is the predominant mechanism. However, cations can also be removed by adsorption in the pores of aluminosilicate systems and, in general, adsorption is greater than ion exchange when the cations to be removed are present in excess compared to the cationic exchange capacity of the zeolite. This is the Donnan equilibrium that is also observed when using resins.

The pH of the water to be treated is the preponderant factor in the yield of ions to be removed. In general, zeolites are amphoteric and tend to neutralise waters, by acting as a proton acceptor or as a proton donor. During adsorption of metal cations,  $H^+$  ions participate in many reactions in the aqueous and solid phases and are exchanged as a function of the retained or released cations. Protonation or deprotonation occurs on the surface according to the following equilibria:

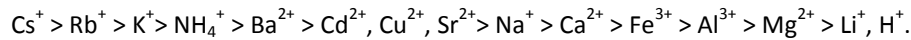


(S represents either Si or Al)

The temperature of the water to be treated plays an important role in the ion exchange mechanism. Its efficacy is greater at high temperatures (50°C) due to more rapid reaction kinetics.

### 1.3.4. Use for treating water intended for human consumption

Clinoptilolite is mainly used for removing  $\text{NH}_4^+$  ions. The selectivity of this zeolite in regard to the main cations is as follows:



To remove  $\text{NH}_4^+$  ions, the pH must be lower than or equal to 7. The regenerating agent most commonly used for this type of zeolite is sodium chloride.

Caesium and rubidium ions are bound irreversibly and regeneration is thereby impossible. This causes serious problems when these elements are radioactive. Clinoptilolite can be used to remove these radioelements.

Commercial zeolites are in most cases natural zeolites that have been modified or, more rarely, are synthetic, and sold in the acid ( $\text{H}^+$ ),  $\text{NH}_4^+$  or  $\text{Na}^+$  forms. It has been shown that clinoptilolite and chabazite are more efficient after being treated with NaOH, particularly for removing  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  and, in this case, the exchange capacity can reach 100 mg/kg.

To synthesise or modify zeolites, chemical methods or physico-chemical methods are used.

The chemical methods are used primarily to 'stimulate' natural zeolites to improve their selectivity, their specific surface and thus their exchange capacities. To do so, the stimulating metal salt is combined with a basic solution (usually sodium hydroxide or potassium hydroxide at high concentrations (5 to 10 M)) and put in contact with the zeolite. Iron-modified clinoptilolite has been used to remove manganese ( $\text{Mn}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), zinc ( $\text{Zn}^{2+}$ ) and arsenic.

Physico-chemical methods are used to synthesise aluminosilicates from solutions of silicon or aluminium salts.

## 2. Properties of ion exchangers

### 2.1. Selectivity

Ion exchangers are characterised by their exchange capacity and exchange constant.

For example, and in the case of cation resin in acid ( $\text{H}^+$ ) form, put in contact with a NaCl solution,  $\text{H}^+$  ions in the resin are exchanged with  $\text{Na}^+$  ions in the solution, according to the following equilibrium:



with an exchange constant between  $\text{H}^+$  and  $\text{Na}^+$  ions equal to

$$K_{\text{H/Na}} = \frac{[\text{Na}^+]_r \cdot [\text{H}^+]_s}{[\text{Na}^+]_s \cdot [\text{H}^+]_r}$$

For a strong acid exchanger  $\text{Na}^+ > \text{H}^+ \Rightarrow K_{\text{H/Na}} > 1 \Rightarrow \log K_{\text{H/Na}} > 0$

For a weak acid exchanger  $\text{Na}^+ < \text{H}^+ \Rightarrow K_{\text{H/Na}} < 1 \Rightarrow \log K_{\text{H/Na}} < 0$

Considering the exchange between a  $\text{H}^+$  ion and a monovalent ion  $\text{M}^+$  gives

$$K_{\text{H/M}} = \frac{[\text{M}^+]_r \cdot [\text{H}^+]_s}{[\text{M}^+]_s \cdot [\text{H}^+]_r}$$

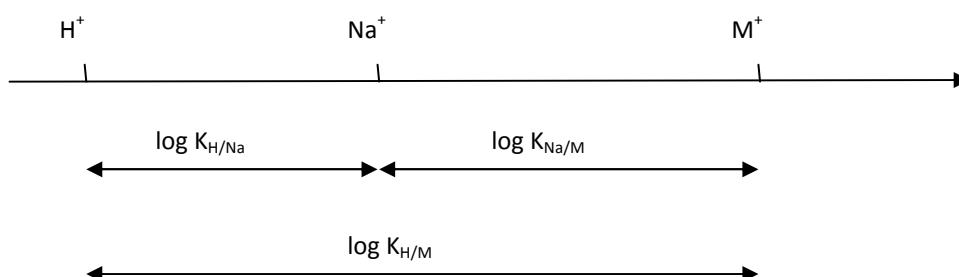
Considering the exchange between a  $\text{H}^+$  ion and a monovalent ion  $\text{M}^+$  gives

$$K_{\text{Na/M}} = \frac{[\text{M}^+]_r \cdot [\text{Na}^+]_s}{[\text{M}^+]_s \cdot [\text{Na}^+]_r} = K_{\text{H/M}} / K_{\text{H/Na}}$$

$$\text{or } \log K_{\text{Na/M}} = \log K_{\text{H/M}} - \log K_{\text{H/Na}}$$

As the logarithms of exchange constants are additive, it is possible to represent them on a linear scale and the distance between the log of the constants of two given ions is thus the log of the constant between these two ions.

**Figure A2: Affinities on a logarithmic scale**

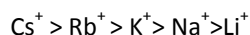


It is therefore possible to establish logarithmic scales of affinity for ions of the same valence, such as presented in Figure 2.

*Note:* for ions of different valence and on strong acid resins (stoichiometries different from 1:1), equilibria also depend on concentration.

The forces that act on the ion group of a resin and the ion to be removed are generally electrostatic. The affinity of the resin for different ions determines its selectivity. In general, the following selectivity rules can be established:

- **a strong exchanger preferentially binds ions with the highest charge.** This is an electrostatic effect.  
For example,  $\text{Fe}^{3+}$  binds better than  $\text{Cu}^{2+}$  which binds better than  $\text{NH}_4^+$ .
- **a strong exchanger preferentially bind ions that have, at equal concentration and charge, a relatively small volume in the hydrated state.** Affinities can be ordered thusly:

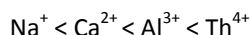


which is the order in which the radius of the hydrated ion increases;

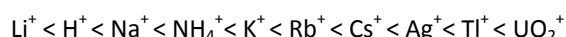
- **a weak exchanger preferentially binds ions that form strong bonds with the ion functional group (on the resin).** Thus, an ion-exchange resin with a carboxyl functional group ( $-\text{COO}^-$ ) and a stoichiometry of 1:1 will have a higher affinity for protons than for a metal ion. A chelating resin will also show a preference for metals that form stable complexes with the attached functional group:



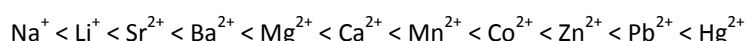
For an cation-exchange resin with a sulfonic functional group and a stoichiometry of n:1, affinity increases with charge:



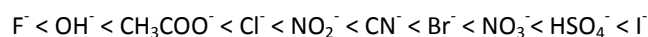
and for a given charge, affinity increases with atomic mass and/or molar mass (ammonium and uranyl ions):



For complexing resins with aminodiacetic groups (EDTA type complexing agents), the order of selectivity is as follows:



For anion-exchange resins with quaternary ammonium groups, the order of selectivity is as follows:



For anion-exchange resins with secondary or tertiary amine groups, the order of selectivity is fundamentally the same but the weakly basic nature of the functional groups confers a high affinity for  $\text{OH}^-$  ions.

## 1.2. Distribution coefficients

The exchange constant defines the relative ion affinities for a given exchanger. This is an intrinsic property of the exchanger. The distribution coefficient determines whether a given ion is primarily found in the exchanger or in solution. This is important to know although the distribution coefficient also depends on operating conditions. The distribution coefficient can be deduced from exchange constants and aqueous concentrations. For a given ion, the distribution coefficient is equal to the ratio of concentrations in the exchanger and in solution:  $P = C_r / C_s$ .

Considering the  $H^+ / Na^+$  equilibrium, it can be shown that

$$P_{Na} = \frac{[Na^+]_r}{[Na^+]_s} = K_{Na/H} \cdot \frac{[H^+]_r}{[H^+]_s}$$

$$\log P_{Na} = \log K_{Na/H} + \log [H^+]_r - \log [H^+]_s$$

If the exchanger is only in the  $H^+$  form, then

$$\log [H^+]_r = C_e \text{ (exchange capacity); moreover } -\log [H^+]_s = \text{pH}$$

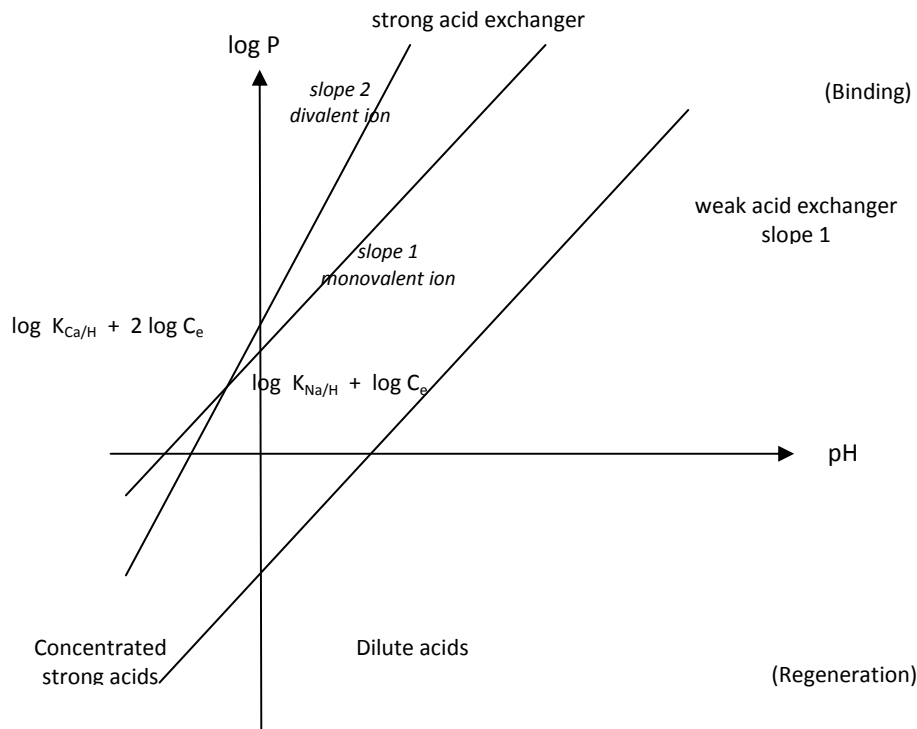
We thus obtain

$$\log P_{Na} = \log K_{Na/H} + \log C_e + \text{pH}$$

For the exchange avec a divalent ion (e.g.  $H^+$  and  $Ca^{2+}$ ), then

$$\log P_{Ca} = \log K_{Ca/H} + 2 \log C_e + 2 \text{ pH}$$

**Figure A3 : Trends in the logarithm of the distribution coefficient as a function of pH**



Trends in the logarithm of the distribution coefficient as a function of pH (see Figure A3):

- Strong acid resin ( $\log K > 0$ ); slope is equal to the charge of the ion. Regeneration with  $\text{H}^+$  ions is difficult;
- Weak acid resin ( $\log K < 0$ ); slope always equals 1. No binding in acidic solutions. Regeneration with  $\text{H}^+$  is easy.

### 1.3. Permutation of ions

To permute one ion for another, the ion that is to be bound on the resin must have a sufficiently high distribution coefficient ( $P \gg 1$  or  $\log P \gg 0$ ). Two cases are possible:

- the regenerating ion (that is to be bound) has greater affinity for the exchanger than the initial ion. Permutation is quantitative and the initial ion is eluted at the concentration of the incoming ion: this is called **displacement**;
- the regenerating ion has lower affinity for the exchanger than the initial ion: Ion exchange requires a large excess of the incoming ion: this is called **elution**.

## 1.4. Exchange kinetics

### 1.4.1. Plate theory

To study the kinetics of ion exchange in a column, the column is likened to a series of equivalent theoretical plates. A column is thus like a stack of plates, on each of which exchange equilibrium has been reached. Establishing equilibrium takes time and during this time, the solution front has migrated a certain distance in the column that is called the height (h) equivalent to a theoretical plate (HETP). A column of length L will be made up of a number of plates (N) such that  $N = L/h$ . This number of plates determines the efficiency of a column.

Equilibration time directly depends on the exchange kinetics that depends on the plate surface, i.e. the exchanger volume to surface ratio which is a function of  $1/r$  (radius of the resin beads). The equilibration time depends on the thickness of the diffusion layer, i.e. the maximum distance covered by an ion before reaching equilibrium (radius of a bead). It is inversely proportional to this distance and thus also a function of  $1/r$ .

The overall time to equilibrium is thus a function of  $1/r^2$ . Exchange kinetics are thus a function of the inverse of the square of the radius of the beads. This is why finer grained resins are better exchangers. The decrease in the bead diameter is only limited by the loss in charge that it incurs.

### 1.4.2. Determination of exchange fronts

The spread of exchange fronts depends on both exchange constants and exchange kinetics. To represent these fronts on a graph, the simplest solution is to normalise the curves as follows (example of an  $H^+/Na^+$  exchange):

$$y = [Na^+]_r / C_e \text{ and } x = [Na^+]_s / C_0$$

$$1-y = [H^+]_r / C_e \text{ and } 1-x = [H^+]_s / C_0$$

where  $C_e$  is the exchange capacity of the resin and  $C_0$  is the total ion concentration in solution.

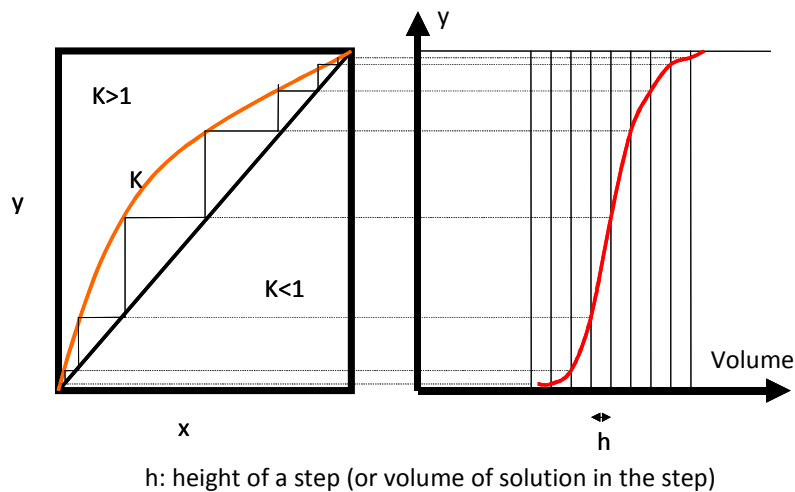
It can be deduced that

$$K = \frac{y \cdot (1-x)}{(1-y) \cdot x}$$
$$\text{And } y = \frac{K \cdot x}{1+x(K-1)}$$

A graphical multistage calculations of HETP can be drawn where  $y = f(x)$ , with x and y having values comprised between 0 and 1.

On these graphs (see Figure A5), the process occurring on the exchange column can be represented as a discontinuous series of 'steps' that symbolise theoretical plates.

Figure A5: Example of a graphical multistage calculation of HETP



A theoretical plate corresponds to the equilibration time, thus the distance travelled in the column as a function of the flow rate.

The proportion of incoming ions can be determined for each plate using this graph and reproduced on a curve giving the saturation rate  $y$  as a function of the volume of the percolating solution. The unit of volume that is used is the volume of an equivalent theoretical plate (height times the section of the column).

The spreading of the exchange front depends thus on thermodynamic equilibria (exchange constant  $K$ , which gives the necessary number  $n$  of plates) and exchange kinetics (height of a theoretical plate). On a column with  $N$  theoretical plates, the exchange front will occur on  $n$  plates. This requires that  $N \gg n$ .

The inflection point of curve  $V_0$  only depends on the total capacity of the column and the ion concentrations in solution.

$$C_{\text{total}} = m \cdot C_e = V_0 \cdot C_0$$

where  $m$  is the mass of the exchanger,  $C_e$  the exchange capacity of the exchanger,  $V_0$  the volume of the solution at the inflection point and  $C_0$  the concentration in solution.

$$V_0 = m \cdot C_e / C_0$$

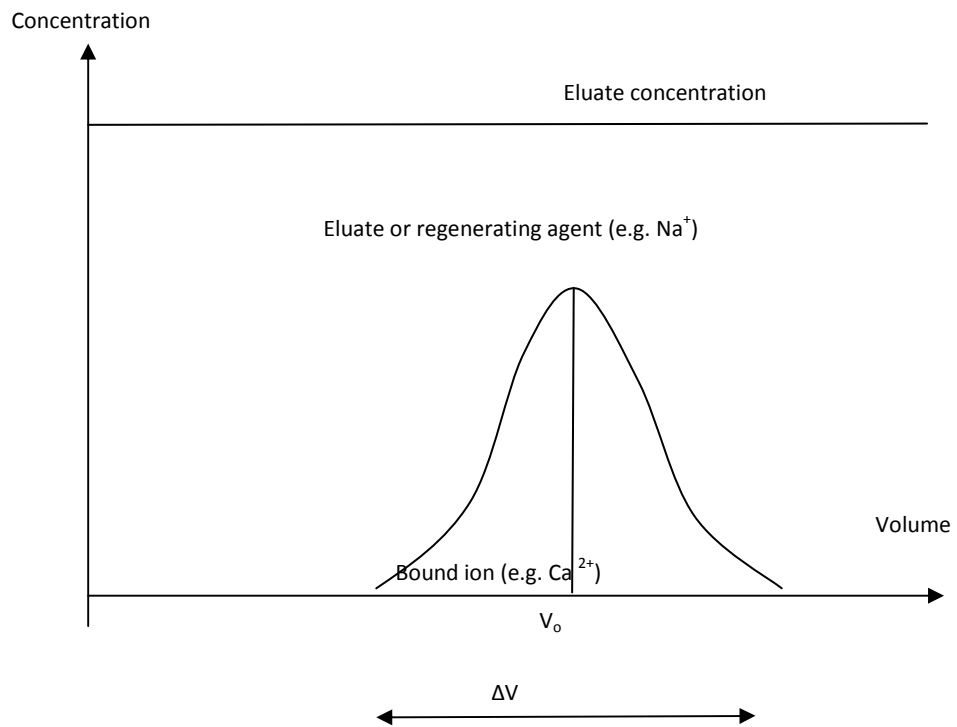
The exchange front spreads more or less as a function of the exchange constant and kinetics. If the velocity of flow in the column is doubled, the height of the plates and thus the spread of the elution curve will also double.

To summarise, the spread of exchange fronts depends on the exchange constant  $K$  which defines the number of plates necessary and the height of each equivalent theoretical plate, i.e. the number and height of the plates.

#### 1.4.3. Shape of elution curves

The position and spread of the elution curves, such as that given in Figure A6, depend on the distribution coefficient ( $P$ ) and the number of equivalent theoretical plates. The volume  $V_0$  (corresponding to the elution peak) for a column containing a mass  $m$  of the exchanger is given by  $V_0 = m \cdot P$  ( $P$  is expressed in litres of solution per exchanger mass). The spread of the elution peak is given by  $\Delta V = 8 V_0 / \sqrt{N}$ . The spread of a peak increases with the distribution coefficient  $P$  and grows narrower with an increasing number  $N$  of theoretical plates in the column (height  $h$  smaller).

**Figure A6: Elution curve**



## **Annex B:**

# **Regulations governing the conditions for the marketing and use of materials and objects that come into contact with water intended for human consumption**

When they come into contact with water intended for human consumption, certain materials and objects used for water treatment and distribution can adversely affect water quality in terms of its organoleptic, physico-chemical or microbiological characteristics and thereby cause water to exceed the tolerable limits and the reference values stipulated by public health regulations, or even lead to health risks for consumers. The marketing and use of these materials and objects are thus regulated.

## **1. Definitions**

The term “materials and objects” includes all the parts used in production plants and distribution systems of water intended for human consumption that supply water without modifying its physico-chemical or microbiological composition. In particular, these include pipes, connectors, coatings, joints, accessories (pumps, valves, taps, etc.), whatever their constituent material (metal, mineral, organic, etc.). They can be manufactured in factories or developed on site, particularly for construction, repair or renovation. The products and objects used for water treatment are therefore not considered to be ‘materials’.

An object is a part that is incorporated into a production plant or distribution system of water intended for human consumption, as it is delivered, and does not require any other part to perform its function. It may consist of one or more components, which themselves can be made up of one or more parts.

A material is a component of a finished product consisting of a basic part. It is characterised by:

- its trade name and its formulation for organic materials (plastics, rubber- or silicon-based elastomers, etc.)
- its trade name, its composition and its generic name in the case of metals or minerals
- Its trade name and its composition for cementitious materials (concretes, mortars).

## **2. Marketing of materials and objects that come in contact with water intended for human consumption**

In compliance with the provision of the French Consumer Code, anyone overseeing the marketing of products must ensure that these products are appropriate for their intended use, meet the current requirements and are not likely to constitute a public health risk. Thus, articles L.121-1 and L.212-1 of the French Consumer Code stipulate that:

*“All advertising comprising, in any form whatsoever, representations, information or presentations which are false or likely to mislead, is prohibited<sup>a</sup>;*

*From their initial market launch, products must fulfil current requirements relating to the health and safety of persons, to fair trade and to consumer protection. The person responsible for the initial launch of a product on a market is, therefore, obliged to check that the latter conforms to current requirements<sup>b</sup> [...]”*

In accordance with the provisions of Article R.1321-48 of the French Public Health Code, *“materials and objects marketed and intended for production plants, distribution systems and treatment plants that come in contact with water intended for human consumption must comply with the specific requirements defined by Ministerial Order issued by the Ministry for Health, with the purpose of ensuring that they are not likely, in normal and*

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<sup>a</sup> Article L.121-1 from the French Consumer Code

<sup>b</sup> Article L.212-1 from the French Consumer Code

*foreseeable conditions of use, to present a danger for human health or bring about an alteration in the water composition defined by reference to set values [...]*

### **3. Use of materials and objects that come into contact with water intended for human consumption**

Article 1321-49 of the French Public Health Code stipulates that *“the person responsible for the production, distribution or treatment of water shall use, in new plants or in partially renovated plants, from the point of water intake to points of compliance defined in Article 1321-5, materials and objects that come into contact with water intended for human consumption that comply with the requirements of Article R.1321-48.”*

Thus, anyone responsible for marketing a material or an object that is intended to come into contact with water intended for human consumption must:

- propose materials and objects that meet the specific requirements laid down in regulations on the group of materials and objects to which the proposed materials or objects belong;
- ensure that all specific requirements concerning the material or object have been met before launching the material or object on the market;
- provide proof at the request of the authorities or customers that the material or object is safe, thereby attesting that the specific requirements have been met.

The provisions of the French Public Health Code apply according to each party's area of responsibility:

- manufacturers marketing materials or objects that are to come into contact with water intended for human consumption as well as operators (retailers, assemblers, etc.) ;
- persons overseeing water production, distribution and treatment.

### **4. Specific requirements regarding groups of materials and objects**

To date, several groups of materials and objects that come into contact with water intended for human consumption have been defined based on their constituent material (metal, mineral, organic or cementitious materials). Implementing Orders of Article R.1321-48 of the French Public Health Code have not yet been issued; the orders and circulars listed in Table XIII thus give the requirements that must be met.

The attestation that specific requirements have been met, given by the Ministerial Order of 29 May 1997 (as amended) regarding materials and objects in permanent production, treatment and distribution plants of water intended for human consumption and its applicative circulars must be obtained by the person who markets the material or object, whatever its constituent material. The nature of the proof that the regulatory requirements have been met for different types of materials is also given in the following table.

### Specific requirements regarding different groups of materials and objects

| Groups of materials and objects constituted of                                                    | Examples                    | Specific requirements                                                                                                                                                                            | Nature of proof that regulatory requirements have been met                                                                                                                                                                                                                                                    |
|---------------------------------------------------------------------------------------------------|-----------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Metal                                                                                             | coatings, alloys, brazes    | Ministerial Order of 29 May 1997 (as amended) <sup>c</sup><br>Annex 1                                                                                                                            | materials certificate                                                                                                                                                                                                                                                                                         |
| Mineral                                                                                           | enamels, ceramics and glass | Ministerial Order of 29 May 1997 (as amended)<br>Annex 2                                                                                                                                         |                                                                                                                                                                                                                                                                                                               |
| Cementitious materials                                                                            | concretes, mortars          |                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                                                               |
| <b>Organic matter</b><br>including 'monomaterials', multilayer or composite materials and objects | plastics, elastomers        | Ministerial Order of 29 May 1997 (as amended)<br>Annex 3<br>and<br>Ministerial Implementing Circulars of 12 April 1999 <sup>d</sup> , 27 April 2000 <sup>e</sup> and 21 August 2006 <sup>e</sup> | ACS <sup>f</sup> issued by one of the laboratories authorised by the Ministry for Health<br>or<br>Compliance with the positive list (CLP) <sup>g</sup> issued by one of the laboratories authorised by the Ministry for Health for pipe-joints of less than 63 mm in diameter, glues, greases and lubricants. |
| <b>Several components</b> also called 'assembled products' or 'accessories'                       | valves, connectors, etc.    | Ministerial Order of 29 May 1997 (as amended)<br>Annexes 1, 2 and 3<br>and<br>Ministerial Implementing Circular of 25 November 2002 <sup>h</sup>                                                 | ACS issued by a laboratory authorised by the Ministry for Health (for accessories involving at least one organic component in contact with water)                                                                                                                                                             |

<sup>c</sup> Order of 29 May 1997 on materials and articles used in fixed installations for production, processing and distribution of water intended for human consumption amended by Orders of 24 June 1998, 13 January 2000, 22 August 2002 and 16 September 2004 (published in the Official Journal of 1 June 1997, 25 August 1998, 21 January 2000, 3 September 2002 and 23 October 2004, respectively)

<sup>d</sup> Ministerial Circulars no. 99/217 of 12 April 1999 and no. 2000/232 of 27 April 2000 on materials used in permanent installations of distribution of water intended for human consumption (published in the Official Bulletin of the Ministry for Health no. 99/25 and 2000/18, respectively)

<sup>e</sup> Circular DGS/SD7A/2006/370 of 21 August 2006 on proof of compliance with health regulations for fibre-reinforced organic materials and finished products that come in contact with water intended for human consumption, with the exclusion of natural mineral water

<sup>f</sup> ACS: Health Compliance Certificate. Assesses the aptness of a material or an article that comes in contact with water intended for human consumption with regard to regulatory requirements. ACSs are delivered for organic materials and objects thereof according to the conditions given in the Circulars of 12 April 1999, 27 April 2000 and 21 August 2006 cited above (Valid for 5 years, can be extended to 10 years for extruded polyethylene tubes).

<sup>g</sup> CLP: Proof of compliance with French positive reference lists (Valid for 5 years).

<sup>h</sup> Ministerial circular no. 2002/571 of 25 November 2002 on the procedures for verifying the compliance with health regulations of accessories and their component parts, composed of at least one organic component that comes in contact with water intended for human consumption

## Annex C:

### Information that a manufacturer must provide when applying for authorisation

Submitted to an authorised institution, the application for authorisation to use resins must contain the following information:

- applicant's name and address
- trade name(s) of the resin concerned by the application
- type of resin (backbone, functional group)
- parameters of water quality that are modified by the resin and its intended use (softening, nitrate removal, decarbonation, etc.)
- description of the manufacturing process for the resin\*
- detailed chemical composition\*: list of commercial substances or preparations with their CAS number, their percentage of use and the names and addresses of suppliers

| Commercial substances or preparations   | CAS number | % weight | Names and addresses of suppliers |
|-----------------------------------------|------------|----------|----------------------------------|
| Monomers and other starting substances: |            |          |                                  |
| Chemical modifiers:                     |            |          |                                  |
| Polymerisation adjuvant:                |            |          |                                  |

- Physical properties\*: density, grain size
- how resins are prepared before use \*(use without any particular preparation, prior percolation with water, etc.)
- Regenerating agents and regenerating conditions \*(in terms of concentration, flow rate, contact time, rinsing, etc.)
- any disinfection procedures that may be employed (product used, concentration, protocol, etc.)
- special conditions of use (avoid strong oxidants, chlorine, etc.)
- authorisations granted in other European Union countries
- if renewing a previously granted authorisation, copy of the previous application
- if renewing authorisation and if necessary, applicants must indicate if they have initiated a request for the registration of the non-compliant substance(s) on official positive lists, if they have replaced it (them) with substances already appearing on the positive lists or if there is no change in substances used.

\* if this information were to change, the applicant must inform — in writing — the institution in charge of health inspections.

**Annex D:**  
***A minima* list of volatile organic compounds (halogenated or non-halogenated) that must be screened for**

| Parameter                          | Testing standards |
|------------------------------------|-------------------|
| Benzene µg/L                       | NF EN ISO 11423-1 |
| Toluene                            | NF EN ISO 11423-1 |
| Ethylbenzene                       | NF EN ISO 11423-1 |
| Xylenes ( <i>m</i> - + <i>p</i> -) | NF EN ISO 11423-1 |
| <i>o</i> -Xylene                   | NF EN ISO 11423-1 |
| 1,2,3-trimethylbenzene             | NF EN ISO 15680   |
| 1,2,4-trimethylbenzene             | NF EN ISO 15680   |
| 1,3,5-trimethylbenzene             | NF EN ISO 15680   |
| Isopropylbenzene                   | NF EN ISO 15680   |
| <i>trans</i> -1,2-dichloroethylene | NF EN ISO 10301   |
| 1,1,1-trichloroethane              | NF EN ISO 10301   |
| 1,1,2-trichloroethane              | NF EN ISO 15680   |
| 1,1-dichloroethane                 | NF EN ISO 15680   |
| 1,1-dichloroethylene               | NF EN ISO 10301   |
| 1,2-dichloroethane                 | NF EN ISO 10301   |
| <i>Cis</i> -1,2-dichloroethylene   | NF EN ISO 10301   |
| Bromochloromethane                 | NF EN ISO 10301   |
| Bromoform                          | NF EN ISO 10301   |
| Chloroform                         | NF EN ISO 10301   |
| Dibromochloromethane               | NF EN ISO 10301   |
| Bromodichloromethane               | NF EN ISO 10301   |
| Tetrachloroethylene                | NF EN ISO 10301   |
| Carbon tetrachloride               | NF EN ISO 15680   |
| Trichloroethylene                  | NF EN ISO 10301   |
| Acetone                            | XP P 41-250-2     |
| Butanone                           | XP P 41-250-2     |
| Methyl isobutyl ketone             | XP P 41-250-2     |
| Ethyl acetate                      | XP P 41-250-2     |

## Annex E: Measuring the chlorine demand

Chlorine demand in water used to test for migration as laid out in the protocol adapted to standard EN 12873-3 is measured as follows:

1. Take a 100 mL sample of migration water to be tested
2. Adjust the pH to  $7.4 \pm 0.1$  with a buffer free of TOC (and EDTA in particular) such as sodium phosphate, monopotassium phosphate or dipotassium phosphate
3. Add  $1 \pm 0.1$  mg/L of chlorine using a dilute sodium hypochlorite solution
4. Immediately measure the concentration in free chlorine and total chlorine (NF EN 7393-1 or -2)  
=  $C_{0 \text{ test}}$
5. Let sit 1 hour
6. Measure the concentration in free chlorine and total chlorine again =  $C_{1h \text{ test}}$

Perform the same steps for a control water sample

to obtain concentrations  $C_{0 \text{ control}}$  and  $C_{1h \text{ control}}$ .

The chlorine demand of the tested water corresponds to (in %):

$$\left( \frac{(C_{1h \text{ test}} - C_{1h \text{ control}}) - (C_{0 \text{ test}} - C_{0 \text{ control}})}{C_{0 \text{ test}} - C_{0 \text{ control}}} \right) \times 100$$

To validate the measurement of the chlorine demand in the water sample:

- $C_{0 \text{ test}}$  and  $C_{0 \text{ control}}$  must be between 0.9 and 1.1 mg/L chlorine
- the chlorine demand of the control sample must be less than 10% of the starting concentration, or

$$\left( \frac{C_{0 \text{ control}} - C_{1h \text{ control}}}{C_{0 \text{ control}}} \right) \times 100 < 10\%$$

Otherwise, the test needs to be repeated with new samples.

## Annex F: Standard approval form

Name of applicant:

Address of applicant:

Trade name(s) of the exchanger:

Type of exchanger:

Form:

Use(s):

Exchange capacity:

The exchanger "NAME of EXCHANGER" was assessed according to the requirements of the Ministerial Order of "ORDER REFERENCE" as required by the AFSSA report "AFSSA REPORT REFERENCE" by a Laboratory authorised by the Ministry of Health "NAME and ADDRESS of the Laboratory".

Tests were conducted according to standards T90-601 and EN 12873-3.

The exchanger "NAME of EXCHANGER" was tested for the following conditions of use:

|             |  |
|-------------|--|
| Implemented |  |
|-------------|--|

|              | Product | Concentration | Flow rate | Contact time | Rinsing procedure |
|--------------|---------|---------------|-----------|--------------|-------------------|
| Disinfection |         |               |           |              |                   |
| Regeneration |         |               |           |              |                   |

The Laboratory "NAME of LABORATORY" notes that the proof of safety presented by "NAME of APPLICANT" for the exchanger "NAME of EXCHANGER" with regard to its use for treating water intended for human consumption complies / does not comply with the applicable regulatory requirements, subject to the conditions of use defined above.

In conclusion, the Laboratory "NAME of LABORATORY" is issuing a favourable/unfavourable opinion for marketing the exchanger "NAME of EXCHANGER".

Issued at "PLACE" on "DATE"

[Materials] Testing Laboratory Manager "NAME and SIGNATURE"