



Report of the Scientific Committee of the Spanish Agency for Consumer Affairs, Food Safety and Nutrition (AECOSAN) on the use of sodium chloride edible salt obtained from a potassium chloride production by flotation process

Section of Food Safety and Nutrition

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Abstract

The procedures used in Spain for the extraction of salt include a case which uses the purification and crystallization of the salt obtained from the process for the production of potassium chloride by flotation. This process involves an initial stage consisting in the extraction of the raw mineral made up of sodium chloride and potassium chloride and other impurities. After the removal of some of the impurities, the mineral undergoes a flotation process for the separation of potassium chloride involving the use of different reactants, including flocculants, foaming agents and collectors. The salt obtained by means of this procedure between the sixties and the nineties was dumped as useless. Nevertheless, those dumps are currently being used as raw material for obtaining table salt.

The lack of information regarding the specific substances used in the potassium chloride production process, and its potential harmfulness, has created a safety concern. Therefore it has been considered necessary to assess a wide group of substances which may have been used in the process, with the recommendation of the absence of all these substances at levels above reference values, based on toxicological considerations.

Therefore, from the point of view of the potential presence of aliphatic amines and amino alcohols the reference value to establish their absence is 0.3 mg N₂/kg of salt.

For the specific case of the sum of potentially present aromatic amines a reference value for determining their absence is recommended as low as the detection limit of the analytical technique, at maximum of 30 µg of total aromatic amines/kg of salt.

The absence of pine oil residues based on the determination of alpha terpineol must be established, at minimum, at a level of 1 µg/kg of salt.

Key words

Salt, sodium chloride, potassium chloride, flotation.

1. Introduction

In Spain, the extraction, distribution and sale of salt and edible brine is governed by Royal Decree 1424/1983 (BOE, 1983), which aims to define, in legal terms, what is meant by salt and edible brine and to establish, on a mandatory basis, the standards for these products, the technical and health conditions that shall be fulfilled by the industries engaged in the manufacture, preparation and/or mixture of the same, together with the conditions of hygiene in the preparation and packaging, where applicable, and to establish the conditions to which the storage and transport of the product are subject.

Although the *Codex* Standard for food grade salt (*Codex Stan 150-1985*) expressly excludes in the scope of its application salt obtained from sources other than those listed in Section 2 of this standard, in particular any salt which is a sub product of the chemical industries, at present there are no legal restrictions at national level with respect to the extraction of edible salt from chemical processes, the recovery from brines, salts, fishing or other industrial uses.

The procedures used in Spain for the extraction of salt include a case which uses the purification and crystallization of the by-product obtained from the process for the production of potassium chloride by flotation. This process involves an initial stage consisting in the extraction of the raw mineral made up of sodium chloride and potassium chloride and other impurities. After eliminating some of the impurities the mineral undergoes a flotation process for the separation of potassium chloride involving the use of different reactants, including flocculants, foaming agents and collectors. Initially the salt obtained in this procedure between the sixties and the nineties was dumped as useless. Time after, the commercial development of the dumps for its use as edible salt was started.

The salt obtained in this process must comply with the characteristics established in article 13 of Royal Decree 1424/1983, approving the Technical and Health Regulations on the extraction, distribution and sale of salt and edible brines if it is intended for use in human food. Nevertheless, given that each process involves the use of a baseline mineral which may contain various impurities, requiring the use of different reactants in the flotation process and although the available information on the reactants used then in the production of potassium chloride is limited, the control authorities consider it necessary to assess whether the extracted salt may contain residues derived from this production process which may pose a risk to the health of consumers and which are not governed by Royal Decree 1424/1983.

Consequently, the Management Board of the Spanish Agency for Consumer Affairs, Food Safety and Nutrition (AECOSAN) has asked the Section of Food Safety and Nutrition of the Scientific Committee to carry out an assessment regarding the safety for use as food and for the treatment of the water used of the salt obtained from a process to extract potassium chloride by flotation.

2. Process for the extraction of edible salt

The process for the extraction of edible salt, the assessment of which has been requested by the AECOSAN, consists of two main stages:

- Extraction and separation of sodium chloride.

- Dilution, purification and crystallisation.

2.1 Extraction and separation of sodium chloride

The process for the extraction of sodium chloride starts with the extraction of a raw mineral (called sylvinite) made up mainly of potassium chloride, sodium chloride and magnesium chloride.

After extraction, the mineral undergoes a two-stage process:

- The objective of the first stage is to obtain a mineral with characteristics that permit the good separation of the sodium and potassium chlorides. Therefore, the raw mineral, measuring more than 5 mm, is dry milled, and then a saturated solution of sodium and potassium chlorides (mother liquors) are added. These function, as they are saturated, as a vehicle of transport. The composition of the mother liquors is: potassium chloride (100 g/l), sodium chloride (204 g/l) and magnesium chloride (50 g/l).

Next, the mineral is sieved and ground (rod mills) to reduce the size of the particles to less than 1 mm.

Then the majority of the insoluble impurities are eliminated. To do so, the mineral is shaken hard in separation cells until the insoluble particles attached to the sodium chloride and potassium chloride particles are separated. The resultant pulp is made up of clays and sodium and potassium chlorides which are separated into bioseparation tanks in which the larger particles (mineral consisting mainly of sodium and potassium chloride) sediment and are separated from the finer particles (insoluble clays).

The separated mineral, rich in sodium and potassium chloride is again subjected to a washing process using classifiers and hydrofoaming agents so that any remaining clay particles are eliminated, leaving a mineral with a granulometry of less than 1 mm and mainly consisting of sodium chloride and potassium chloride.

- The second stage consists in the separation of the sodium chloride and the potassium chloride using a flotation process. This process requires the use of a flocculent or depressant (potato or corn starch), the function of which is to agglutinate any micro-particles of clay that may still be present in the mineral and make them sediment, a foaming agent (pine essential oil) to give consistency to the air bubbles in the centre of the flotation pulp and a collector agent (ammonium compounds) the function of which is to cover the particles of potassium chloride making them aerophylic and hydrophobic. This, in turn, makes the particles of potassium chloride attach themselves to the air bubbles formed and they move towards the surface of the flotation cell where they are recovered mechanically in pulp form together with the foaming agent and the collector.

At the same time, the sodium chloride particles sediment in pulp form to the bottom of the flotation cell. This pulp undergoes a washing and filtration process to eliminate the liquid part which is recirculated to the mother liquor circuit. The solid mineral obtained (mainly sodium chloride) is deposited in the open air. Afterwards, it is dissolved, purified and crystallized to be used in human consumption.

2.2 Dilution, purification and crystallisation

The sodium chloride is obtained by crystallisation of the dissolved salt, using an evaporator.

- Stage 1. The sodium chloride deposited is mixed and dissolved with a condenser to form saturated brine. The insoluble material is left at the bottom of the tank and eliminated from there. The saturated brine is filtered using a deep sand bed filter in order to reduce the quantity of insoluble material to less than 50 ppm. This brine is taken to storage tanks before going to stage 2.
- Stage 2. The saturated brine is evaporated in a system of heat exchangers, provoking the precipitation of the salt crystals (mainly sodium chloride and some calcium sulphate). The calcium sulphate crystals are separated as they are smaller in size, and the majority of the liquid phase of the salt crystals is eliminated using a centrifugal process, obtaining a humidity of approximately 2.5 %.

Auxiliary stages

- Stream of water from the process. A closed circuit of water is used in the process. The steam generated in the evaporators through which the saturated brine, the salt of which precipitates, is treated, compressed and overheated to be reused as a heating fluid in the heat exchanger. These condensed vapours are cooled and used to dissolve the salt of the raw material resulting from the potassium chloride flotation process. In this way, the water returns to the concentrator and the cycle starts again.
- The purge from the concentrator containing the smallest crystals of calcium sulphate is decanted in order to separate the crystals from any possible undissolved mineral species.

3. Potential risks

The use of the sub-product from the flotation of potassium chloride for the extraction of food salt entails specific different risks with respect to the general risks that may exist in the food salt extraction process, the potential presence of traces of amines used as collector agent and of pine essential oil used as a foam stabilising agent. It should also be noted that most of the amines and pine essential oil is expected to be removed together with the foam containing the potassium chloride.

The above residues would remain in the saturated liquid stage in the centre of which the salt crystals precipitate. These crystals are separated from the saturated brine until humidity levels of approximately 2.5 % are reached. Next, the salt is dried before packaging, and consequently some of the residues present in the brine may be present in the dry salt.

The fact that a closed circuit of water, containing the potential amine and pine essential oil residues, is used implies that there would be a process concentrating the potential residues and, therefore, an increase in the risk of their presence in the salt which is finally obtained.

In any case, the probability of finding amine and pine essential oil residues in the flotation process is considered to be low for the following reasons:

- The majority of amines and essential oil used is expected to be eliminated together with the

potassium chloride in the flotation process, and their presence in the residue used in the food salt extraction process to be very small.

- The quantity of liquid remaining in contact with the pure crystals of sodium chloride in which traces of amines and pine essential oil might be detected is very small.

In this respect, it is considered that in order to guarantee the safety of the edible salt obtained from a potassium chloride production by flotation process the following aspects should be controlled in the final product:

1. The absence of residues of the amines used as a collector in the flotation process. The residues should be below a detection level considered as toxicologically safe.
2. The absence of traces of pine essential oil below a detection level considered as toxicologically safe.

4. Reference value proposal

The absence of residues of amines and pine essential oil must be determined using techniques with a suitable detection limit that ensures, at minimum, the detection of levels of toxicological interest which, in the context of this report, are called the reference values.

4.1 Residues of amines

The flotation process normally uses long-chain primary amines which contain between 12 and 24 carbon atoms in the aliphatic chain (Searls, 1990) such as for example octadecylamine hydrochloride (ODA) and dodecylamine hydrochloride (DDA) (Millet and Yalamanchi, 1994) (Cao et al., 2010).

Nevertheless, and given that in this case the type of amine used as a collector is unknown, it is considered necessary to evaluate two groups of amines based on their toxicity: aliphatic amines and amino alcohols on the one hand, and aromatic amines on the other.

In the case of the aliphatic amines, octadecylamine (ODA) is representative of this group in terms of toxicity. In this respect, Decichmann et al. (1958) established for octadecylamine a NOAEL (Non Observable Effect Level) of 500 ppm (25 mg/kg b.w./day) following a toxicity study carried out over 2 years on Sprague-Dawley rats and a NOAEL of 3 mg/kg b.w./day in the case of a study carried out on dogs for 1 year. In the case of the study on rats, the European Chemicals Agency subsequently lowered the NOAEL to 200 ppm (10 mg/kg b.w./day) (ECHA, 2011), considering the existence of adverse effects to the dose of 500 ppm established by Diechmann et al. (1958).

Taking the lowest established NOAEL as the base level (3 mg/kg b.w./day) a Tolerable Daily Intake (TDI) can be estimated for octadecylamine of 3 µg/kg b.w./day applying a safety factor of 1 000, given the limitation of the existing data.

On the basis of the estimated TDI, a reference value can be established for the octadecylamine residues, considering the estimated intake of salt that may contain residues of octadecylamine. In this respect, although the World Health Organisation recommends that the daily salt intake

in adults is not higher than 5 g, the European Commission has indicated that the true intake in Europe is substantially higher (from 8 to 12 g/person day) (EC, 2012).

Therefore, considering an estimated TDI of 3 µg/kg b.w./day, a maximum intake of salt in Europe of 12 g/person day and a body weight of 60 kg in adults, a reference value can be established for the residue of octadecylamine of 15 mg/kg of salt:

$$\text{Reference value} = \frac{3 \mu\text{g}}{\text{kg} \times \text{day}} \times 60 \text{ kg} \times \frac{1 \text{ day}}{12 \text{ g salt}} = 15 \mu\text{g/g} = 15 \text{ mg ODA/kg of salt}$$

In addition, Royal Decree 1424/1983 establishes in its article 13 that the content of nitrites, nitrates and ammonium salts shall not exceed, expressed in nitrogen, 20 mg per kilogram of salt, except in the case of nitrate salts (BOE, 1983). In this respect, analytical methods exist for determining nitrogen in salt with a quantification limit of 0.3 mg N₂/kg of salt.

Considering the molecular weight of octadecylamine (C₁₈H₃₉N, M.W.= 269 g/mol) and of molecular nitrogen (N₂, M.W.= 28 g/mol), the estimated reference value for octadecylamine can be expressed as a function of the molecular nitrogen content:

$$\text{Reference value} = \frac{0.015 \text{ g ODA}}{\text{kg salt}} \times \frac{28 \text{ g N}_2/\text{mol}}{269 \text{ g ODA/mol}} = 1.6 \text{ mg N}_2/\text{kg of salt}$$

Therefore, with respect to the possible octadecylamine residues and considering the availability of test methods, the reference value for the detection of octadecylamine can be established at 0.3 mg N₂/kg, equivalent to an estimated daily intake of ODA <20 % of the TDI. Consequently, the limit of 20 mg of N₂/kg of salt established under Royal Decree 1424/1983 is not considered sufficient as a reference value for the detection of possible octadecylamine residue in salt.

The other group of amines to be evaluated, considering the worst-case scenario, is that of aromatic amines.

Within this type of amine, 2-naphthylamine (2-NA) has been considered by the IARC (International Agency for Research on Cancer) as carcinogenic (group 1) (IARC 2010). Furthermore, the OEHHA (Office of Environmental Health Hazard Assessment) has established for 2-naphthylamine a NSRL (No Significant Risk Level for Carcinogens) of 0.4 µg/day (OEHHA, 2002).

Considering the NSRL for 2-naphthylamine of 0.4 µg 2-NA/day and a daily intake of salt of 12 g/day (EC, 2012), a reference value can be established for the detection of residues of 2-naphthylamine of 0.033 mg/kg of salt.

From the point of view of the possible presence of aromatic amines, the sum total of aromatic amines present in the same should be less than 30 µg/kg of salt.

4.2 Residues of pine essential oil

As indicated above, another aspect to consider in order to guarantee the safety of edible salt obtained from a potassium chloride production by flotation process is the absence of traces of pine essential oil below a detection level considered toxicologically safe.

Considering a NOAEL of 50 mg/kg b.w./day for pine oil (EPA, 2006) a reference value can be established, as for the case of octadecylamine, for the detection of the pine essential oil residues of 250 mg/kg salt, equivalent to a value 700 times higher than the olfactive threshold of one of the main components, alpha terpineol (330-350 µg/kg) (Leffingwell, 2015) and therefore a simple olfactive detection would be far below the potentially toxic levels. It is also noted that, in accordance with that established in Regulation (EC) No 1334/2008, the use of alpha terpineol is authorised as a flavouring agent in food in accordance with good manufacturing practices (EU, 2008). In addition, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) establishes that there is no safety concern with respect to the use of alpha terpineol as a flavouring agent (JECFA, 1998).

Consequently, the reference value to consider for the determination of the presence of alpha terpineol, considering the availability of test methods would be 1 µg/kg of salt.

Conclusions of the Scientific Committee

The lack of information regarding the specific substances used in the potassium chloride production process, the subject of this report, creates uncertainty. Therefore it would appear necessary to assess a wider group of the substances which may have been used and recommend the control of the absence of all these substances at levels above the reference values for their determination based on toxicological considerations.

Therefore, from the point of view of the potential presence of aliphatic amines and amino alcohols the reference value to establish their absence is 0.3 mg N₂/kg of salt.

For the specific case of the sum of potentially present aromatic amines, a reference value for determining their absence is recommended as low as the detection limit of the test technique permits and, at maximum, of 30 µg of total aromatic amines/kg of salt.

The absence of pine oil residues based on the determination of alpha terpineol must be established, at minimum, at a level of 1 µg/kg of salt.

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