

ANIS : Algae for naturally iodized salt
Feasability of using seaweeds to combat the iodine deficiency.

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The feasibility of a naturally iodized salt, using a seaweed ingredient, was demonstrated. Two seaweeds, in accordance with the regulation constraints and their iodine level, were selected for the final studies : a red algae, *Gracilaria verrucosa*, and a brown algae, *Laminaria hyperborea*. Designed ingredients from these seaweeds permitted to elaborate an original process for the preparation of the blend seaweed ingredient/salt in accordance with the major constraint of the regulation : to guarantee a constant level of iodine in the blend and to prevent segregation between the salt and the seaweed ingredient. The stability studies demonstrated a constant level of iodine in the seaweed ingredient, and in the iodized salt, stored in different conditions. The consumer acceptance of the designed iodized salt is good and the clinical studies demonstrated an equal bioavailability of the iodine from algae in comparison with potassium iodide.

1. INTRODUCTION

Iodine is essential for the synthesis of thyroid hormones, playing a decisive role in cellular metabolism, in the process of early growth and development of most organs, especially the brain [1,2,3]. Recent surveys showed that 1,572 million human beings are still living in conditions of iodine deficiency [4]. Therefore, iodine deficiency constitutes the principal cause of potentially preventable mental retardation in the world. In

Europe, 150 million human beings are concerned [5,6]. All the European countries (except five of them) suffer from marginal to severe iodine deficiency, particularly Portugal, Spain, Italy, Roumania, Bulgaria and Hungary.

In Europe and most Western countries, the main source of dietary iodine is seafood including fish and shellfish [8]. However, even a regular consumption does not guarantee an adequate iodine supply. The major procedure used to correct iodine deficiency is Universal Salt Iodization (USI) by addition of iodide and iodate [9].

Programmes of salt iodization are, when properly applied, extremely efficient and cheap. Failures of implementation of such programs were frequently reported, even in Europe [5]. In Germany for example, despite the iodization of salt, one third of the newborn babies have an enlarged thyroid and struma surgery causes costs of about 2 billion German Marks per year.

One of the numerous reasons for failure of USI programmes has been the reluctance, or even the opposition by some bodies and governments, to add iodine as an artificial additive to salt. It must also be emphasized that an important fraction of European consumers generally favour natural products over artificial ones. The leading companies in the field of table salt encounter difficulties in promoting and marketing standard iodized salts.

Seaweeds have an extremely high iodine content : as an example, certain seaweeds contain 1 000 times as much iodine as cod, an average iodine-containing fish [10, 11]. Seaweeds do not constitute a staple diet for humans in Western countries [10]. However, one is allowed to consume seaweeds in different European countries, including France, which has designed a specific regulation for edible seaweeds [11].

The objective of our work was to demonstrate the industrial feasibility of a naturally iodized salt using a seaweed ingredient as source of iodine. In this paper we present the major results of our work : the iodine content in seaweed, the stability studies on iodine in seaweeds and in iodized salts, the consumer acceptance and the bioavailability results.

2. METHODS

2.1. Seaweeds supplying and preparation

The two selected seaweeds, because of their low heavy metals level, are *Gracilaria verrucosa* (red seaweed) and *Laminaria hyperborea* (brown seaweed). Those seaweeds were collected on the « Pen Lan » site, near CEVA, in the north of Brittany (France), in front of the Bréhat Island. The seaweeds were washed with seawater, before drying at low temperature (50°C) and grinding to a size inferior to 120 microns.

2.2. Iodine measurement in seaweeds

The method is based on the Food Chemical Codex method [7] :

- ashing of seaweeds in the presence of K_2CO_3 (weight ratio K_2CO_3 /seaweed = 5/1) at 600°C ;
- recovery of the ashes in boiling water ;
- transformation of iodide into iodate by additionning bromide in acid medium ;
- addition of KI and titration of iodine by a sodium thiosulfate solution.

2.3. Iodine measurement in salts

The analytical method is similarly based on the Food Chemical Codex with, in a first step, a melting of the sample, in presence of K_2CO_3 . Iodine measurement in urines is performed by alkaline ashing and determination of iodine level by the Sandell & Kolthoff reaction.

2.4. Preparation of iodized salts with seaweeds

The method is confidential and under patent publication. The process permits to guarantee a constant level of iodine in the blend, without segregation. The iodized salts with iodide or iodate are prepared by solution addition before dehydration.

2.5. Study of iodine stability in seaweeds and iodized salts

Seaweed meals samples were stored in closed plastic boxes at room temperature. Five measurements of iodine were performed at different times.

Study of iodine stability in iodized salts (with seaweed, iodide an iodate) were carried on during 180 days. Two storage conditions were used : soft conditions, cycle of 12 hours at 10°C / 78% relative humidity (RH) followed by 12 hours at 30°C / 22% RH and « tropical » conditions, cycle of 12 hours at 40°C / 60% RH followed by 12 hours at 40°C / 99% RH. Different commercial packagings were used in those stability studies.

2.6. Consumer acceptance

8 prototypes (see table 1) of seaweed-iodized salts have been elaborated, with 3 different species of seaweed, ground to different particle sizes. The sensorial tests aimed at determining which prototypes show the best potential to partially substitute the classical iodized fine salt. As the objective of the study was mass diffusion of a seaweed-iodized salt, the reference for the tests is ordinary table fine salt. The evaluation gave information on the consumption habits and the socio-demographic profile of the participants. The smell and the taste were each evaluated through 40 discrimination triangular tests with open question on preference. The visual aspect was evaluated through 320 tests of classification based on preference.

Table 1
Seaweed iodized salts prototypes

	Salts containing visible seaweed particles	Salts appearing homogeneous (without visible particles)	
Parti- cles more and more nume- rous	<i>Gracilaria verrucosa</i> $d < 80 \mu\text{m}$ Particles are scarce, of small size, not very visible	<i>Laminaria hyperborea</i> $d < 80 \mu\text{m}$ Off-white color (very light)	Color darker and darker
	<i>Laminaria hyperborea</i> $280 \mu\text{m} < d < 630 \mu\text{m}$ Particles are more numerous, fine, green, visible	<i>Laminaria hyperborea</i> $d < 120 \mu\text{m}$ Creamy color (light)	
	<i>Gracilaria verrucosa</i> $280 \mu\text{m} < d < 630 \mu\text{m}$ Particles are rather numerous, elongated, black, well visible	<i>Gracilaria verrucosa</i> $d < 120 \mu\text{m}$ Pinkish beige color (light)	
	<i>Ascophyllum nodosum</i> $280 \mu\text{m} < d < 630 \mu\text{m}$ Particles are very numerous, green, fine, well visible	<i>Ascophyllum nodosum</i> $d < 80 \mu\text{m}$ Beige color (darker)	

2.7. Bioavailability studies of seaweed iodine

Two clinical studies were performed on human volunteers : one in Brussels and one in Marseille. The bioavailability of iodine in seaweeds was measured by the ratio of iodine intake (2000 μg) and iodine

excretion in the urines (48 hours after intake), after measurement of the iodine status for each volunteer. Each volunteer absorbed iodine under the form of seaweed meal and iodide.

3. RESULTS AND DISCUSSION

3.1. Iodine in seaweeds

One characteristic of the seaweeds in comparison with land vegetables is the high iodine level. Usually the highest values of iodine are found in the seaweed family « Phaeophyceae » or brown seaweeds. In this family, the highest values are observed for the *Laminaria* species : between 5000 and 7000 mg/kg on the dry weight.

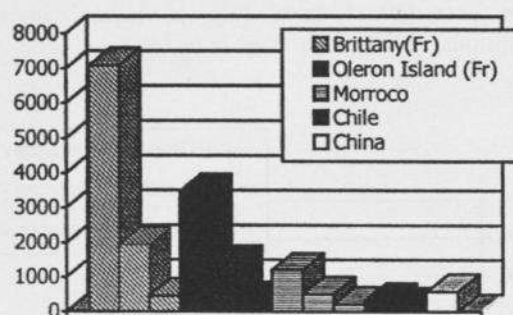


Figure 1. Iodine content in commercial *Gracilaria* sp. (mg/kg dry matter)

Commercial samples obtained from European suppliers (France, Norway) allow to confirm the high value of iodine on the selected brown seaweed *Laminaria hyperborea*. The observed values are found between 5500 and 7000 ppm on the dry weight. This seaweed is the most collected in Europe, particularly in Norway, for the production of alginates. Presently, more than 200 000 tons are collected per year.

Besides, the iodine levels observed in the red seaweed *Gracilaria verrucosa* are very different, depending on the place of collecting, as shown on figure n°1. Usually, the level observed are near 500 ppm (Chile or China). But apparently, our studies show the possibility to find high values of iodine in this seaweed, in Brittany, or in the Oléron Island (France - Atlantic) and on the coasts of Morocco. *Gracilaria*

verrucosa is used for agar extraction and for human food. The availability of this seaweed is near 30 000 tons (fresh) per year in the world. The two first places producing *Gracilaria verrucosa* are Chile and Asia.

One particularity of the seaweeds is the presence of iodine under both the iodide form and organic forms (mono and diiodothyrosine). The literature reports [12, 13] iodine in brown seaweed is mainly iodide whereas it is mainly organic in red seaweeds.

3.2. Iodine stability in seaweeds

As shown in figure n°2, our experiments permit to demonstrate the high stability of iodine in seaweed meals. For our objectives, this shows the possibility to store seaweeds without loss of iodine, in soft conditions, in watertight bags or boxes.

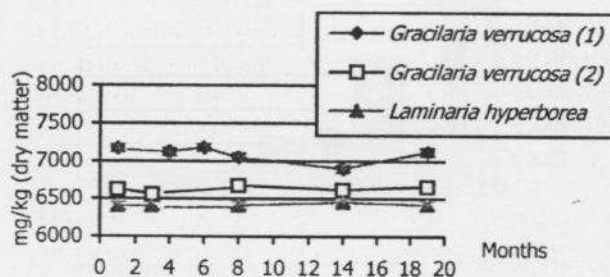


Figure 2. Iodine stability in seaweeds (mg/kg dry matter)

3.3. Iodine stability in iodized salts

In soft conditions (i.e. 12 hours - 10°C / 78 % RH & 12 hours - 30°C / 22 % RH), our studies show that iodine in salts is stable, independantly of the kind of iodine (iodide, iodate or iodine from seaweeds). After 180 days of storage in open cardboard boxes, we do not observe any significant difference between the different mixes.

In more drastic conditions, with high values of relative humidity, we observe differences in the iodine

stability of the salts, related to the packaging and the kind of iodine.

Storage of salt blends, during 180 days, in closed capsules, cardboard boxes with spout (including plastic film), plastic boxes with spout or closed plastic bags (see figure 3), does not cause any loss of iodine during the time. On the contrary, storage in non watertight bags leads to an important loss of iodine (see figures 3, 4 & 5).

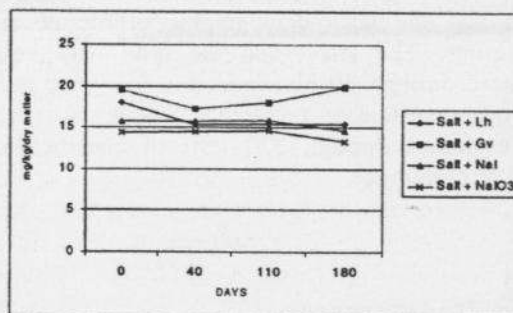


Figure 3. Iodine stability: Storage in closed plastic bags

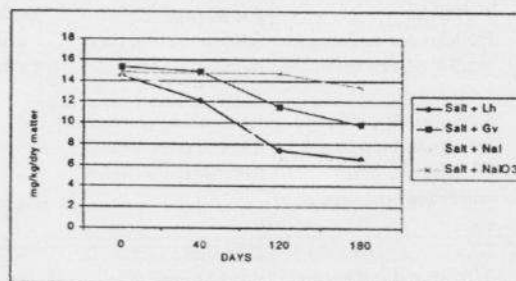


Figure 4. Iodine stability : storage in open cupels

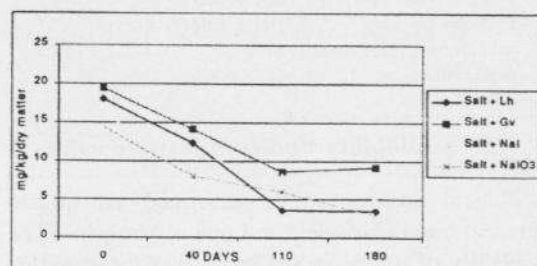


Figure 5. Iodine stability : storage in paper bags

In open cupels, we observe the highest loss of iodine for salts containing iodide or *Laminaria hyperborea*. This seaweed contains a majority of iodine as iodide form. The iodate form is stable. In plastic bags, we observe similar results. Iodide or the *Laminaria hyperborea* form are less stable than iodate or the *Gracilaria verrucosa* form. But unlike with the open capsules, all the blends present high iodine loss. In accordance with the quality and resistance of packaging to the humidity, the storage in cardboard boxes presents a better iodine stability. We do not observe any loss of iodine during the first 120 days.

One hypothesis on the iodine unstability in iodized salts is based on the transformation of iodide or iodate into sublimable molecular iodine. Our results are in contradiction with this affirmation. The loss of iodine depends on the relative humidity in relation with the packaging quality, and the loss of iodine we observe in our experiments is caused by the formation of a brine due to high relative humidity.

Table 2
Urinary iodine in Marseille & Brussels (baseline)

Concentration of urinary iodine ($\mu\text{g/liter}$)	Normal	Marseille	Brussels
Median	100-200	98	62
Range		22-220	8-202
Number of volunteers		149	218
Excretion of urinary ($\mu\text{g/day}$)			
Median	100-200	122	73
Range		56-219	20-182
Number of volunteers		50	70

Table 3
Bioavailability of iodine from seaweeds

<i>Gracilaria verrucosa</i> (% iodine ingested)	Marseille	Brussels
Median	95	85
Range	54-132	24-135
Number of volunteers	8	9
<i>Laminaria hyperborea</i> (% iodine ingested)		
Median	90	61
Range	53-118	18-68
Number of volunteers	8	9

3.4. Consumer acceptance

As for the visual aspect, the presence of seaweed particles is accepted only when they are few and of small size. The color must not be far from a mere off-white. The smell must be discreet and mild. The « marine » or « iodized » smell seems to be pleasant or natural but can easily turn into a negative perception of « tide odour » or « fish odour ». The taste is dominated by the salty sensation and the preference goes to a recognizable taste. It can be a more pronounced salty taste or on the contrary a less aggressive and more perfumed taste.

3.5. Seaweed iodine bioavailability

As expected, table 2 shows that people from Marseille present a better iodine status than people from Brussels. The proximity of the sea and probably the more important consumption of seafood in Marseille are at the origin of these differences. But those data show that these populations present an iodine deficiency. The normality for basis iodine in urine is situated between 100 to 200 $\mu\text{g/l}$.

The data presented in table 3 demonstrate a good bioavailability of iodine from seaweeds. At the first observation, we could conclude that iodine in *Gracilaria verrucosa* is more bioavailable than iodine in *Laminaria hyperborea*.

On the other hand, the weak bioavailabilities observed in Brussels, particularly for iodine from *Laminaria hyperborea* could find an explanation in the complementation of the iodine state of the volunteers (population in Brussels presents an iodine deficiency, table 3).

4. CONCLUSION

Seaweed as a natural ingredient for iodized salt is in accordance with all conditions for industrial exploitation.

Particularly, algal iodine in iodized salts is stable if the packaging is watertight. Our studies show that the iodine potential unstability in salt is more a problem of lixiviation in relation with the packaging resistance to humidity.

On the other hand, the iodine from seaweed is bioavailable and permits to envisage a new class of salt, specialities on market based, on natural ingredient, to combat the iodine deficiency.

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