

Elements for Appreciating the Chemical Characteristics of Portuguese Salt

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ABSTRACT

Commercial salts in Portugal are described including their respective quantities, principal consuming sectors and market trends. The raw salts are differentiated from processed salts (purified, refined, iodized and table salt). The usual laboratory determinations for the chemical characteristics are described together with the methods and equipment used. Analytical results and respective statistical studies for some types are listed. The main purpose of the studies is to improve product quality, intensify the introduction of new technological solutions and to satisfy the requirements of the consumers.

INTRODUCTION

This paper contributes to the definition of the chemical characteristics of the raw and treated salt produced in Portugal.

Crude (raw) salt. Crude or raw salt includes rock and solar salt from sea or saline sources. In the period 1972 to 1976, the productions for rock salt (including brines) was 300,000 t/y; for solar salt, 220,000 t/y.

In the same period the main consumers of rock salt were the chemical and salt refining industry. The uses of marine salt were more varied (Table 1).

Treated salts. According to law, there are four kinds of treated salts: purified (hygienized), refined, table salt and iodized salt.

Purified salt is obtained from sea salt, through washing, centrifugation, thermic drying, milling and screening. It must have the following analytical characteristics:

Loss of mass	maximum 1%
Sodium chloride	minimum 98%
		(in dry product)
Insoluble matters in water	maximum 0.2%
		(in dry product)

Refined salt is produced by refining which consists in recrystallizing rock salt solutions, followed by thermic drying of the product. This type must have a certain number of

properties. It must pass through a mesh of 1.00 mm wide, being the wire of a 0.48 mm diameter. For chemical properties, in aqueous solution of 10% (in weight) it must be a colorless shade and a neutral reaction. The composition shown in Table 2 is compulsory:

TABLE 1

Uses of Salt, 1972-1976

Rock Salt and Solar Salt	Tons/Year
Chemical Industry	316,208
Salt Refining Industry	7,419
Industry of Purification	46,192
Cod Fishing	32,416
Fish Canning Industry	9,484
Chemical Industry	8,049
Salt Preserving	2,558

TABLE 2

Requirements for Refined Salt

Loss of mass	maximum	.20%
Halogens, expressed in Cl^-	minimum	59.7%
Insoluble matters	maximum	.05%
Calcium, expressed in Ca^{++}	maximum	.08%
Magnesium, expressed in Mg^{++}	maximum	.06%
Sulphates, expressed in SO_4	maximum	.30%
Copper	maximum	2.5 ppm
Lead	maximum	5 ppm
Iron	maximum	10 ppm

Table salt, like a refined one, is obtained by recrystallization of rock salt. It must entirely pass the no. 25 ASTM screen 90% (min.) and must be held on the no. 120 ASTM screen. It must contain the properties shown in Table 3. To avoid caking, carbonate of magnesium is added up to 1%.

Use of iodized salt is authorized. Portuguese legislation allows the incorporation of potassium iodide in salt intended for a small area where endemic goiter was detected. The maximum amount permitted is 20 mg/kg. Tricalcic phosphate is added as a stabilizer.

Statistical data. The annual production of treated salts registered a great development. We did a trend-line analysis of its evolution (Table 4). The consumption of iodized salt has kept a relatively constant level (800 t/year). The production of treated salts, in view of coming years, tends to meet the necessities. However, due to conjunctural reasons, some discrepancies in the sub-sectors of refined and table salt are observed.

Purified salt is specially destined for human nourishment (culinary uses), bakery, animal feeding and water softening. Practically all refined salt is absorbed by the textile industry. The table and iodized salts are intended for food.

SAMPLING

Generalities. The characteristics of rock salt are not included in this paper, but are held for another opportunity. For other types, we consider the analytical data available in the Serviço de Sal (Salt Service of the Direcção Geral das Pescas) and the Laboratory of the C.R.P.Q.F. (Comissão Reguladora dos Produtos Químicos e Farmacêuticos).

For sea salt, we took as representative a period of seven years (1970–1976). For treated salts, a period of 13 years (1964–1976) was used. It practically begins when this salt use started about 1964 in this country.

TABLE 3
Requirements for Table Salt

Loss of mass	maximum	.20%
Halogens	minimum	60.0%
Insoluble matters in water	maximum	.03%
Calcium expressed in Ca^{++}	maximum	.04%
Magnesium expressed in Mg^{++}	maximum	.05%
Sulphates expressed in SO_4^{--}	maximum	20%

TABLE 4
Annual Mean Increase in Production

	13 years (1964–1976)	5 years (1972–1976)
Purified salt	4,321 t/y	2,347 t/y
Refined salt	1,063 t/y	1,409 t/y
Table salt	43 t/y	83 t/y

Since the results cover a long period, there is a certain variability, both in the sampling criteria and in the methods of analysis, neither, however, should substantially affect the conclusions.

Sea salt. Samples of 2 kg were collected based on commercial and legal control and technical purposes.

In the second case, the sampling was done to be representative of the different salterns (producing regions) and of the various harvestings.

The samples were taken, as much as possible, in the following conditions: 1) from the interior of crystallizers; 2) after racking and piling the salt on the borders of the crystallizers; 3) from the mounds or the saltworks warehouses; and 4) from the reception warehouses of the purification plants.

When collecting the samples from mounds, we tried to gather them from four zones diametrically opposite and placed at a level of 1.50 m.

Treated salts. Concerning purified salt, the samples were taken from 2×1 bags picked immediately after their packing, or from lots in stock. Other samples were taken, in the plants, immediately after each treatment operation.

The samples of refined salt came from bags utilized for its distribution, i.e., with weights of 25 kg and 50 kg.

When the salt reaches the laboratory, it undergoes a manipulation, according to the current techniques of sampling, in order to get a duly homogenized representative lot.

CHEMICAL ANALYSES

Applied determinations. For crude salt, the tests usually made are loss of mass at 110°C, and (on a dry basis) the 1) insoluble in water, 2) halogens, expressed in NaCl, 3) calcium, expressed in Ca^{++} , 4) magnesium, expressed in Mg^{++} and 5) sulphates, expressed in SO_4^{--} . Lately, we have studied several contaminants (lead, mercury, copper, iron, zinc, chromium and nickel).

For purified salt, it is compulsory by law to determine the loss of mass at 110°C, the insolubles in water and halogens, expressed in NaCl (on a dry basis). The same determinations as mentioned for raw salt have sometimes been carried out.

Either for refined salt or table salt we considered loss of mass at 110°C, and (on a dry basis) 1) insoluble in water, 2) halogens, 3) calcium, expressed in Ca^{++} , 4) magnesium, expressed in Mg^{++} and 5) sulphates, expressed in SO_4^{--} .

Concerning the contaminants, the legal control provides only for the analyses of iron, copper and lead. However, a few determinations are worked out for the other reported cations.

As for iodized salt, the tests were the same as those for purified salt, plus the one for potassium iodide.

Methods used. The determinations were carried out according to the following standards:

Loss of mass. Document ISO/2483.

Insolubles in water. Document ISO/2479.

Halogens, expressed in chlorine. Document ISO/2481 (mercurimetric method). At the CRPQF laboratory we prefer, for ready and economical results, to employ the argentometric method, in the presence of dichlorofluoresceine (Fajans method), the results are practically equivalent.

Calcium and magnesium. Document ISO/2482. The indicator utilized for calcium is the murexide, instead of glyoxal-bis (2-hydroxyanil) (GBHA).

Sulphates. Document ISO/2480.

Iodides. The AOAC method (Association of Official Agricultural Chemists, USA).

Lead. Colorimetric method of the dirizone (diphenyldithiocarbazone).

Mercury. Atomic absorption (FAAS), in a spectrophotometer Perkin-Elmer 403, as per the technique indicated by Perkin-Elmer Corporation, Instrument Division.

Copper. First, we used the sodium diethyldithiocarbamate spectrophotometric method, then, we adopted the zinc dibenzildithiocarbamate method, following the option of the ECSS, who considered it a method to be proposed to ISO (Doc. 117/76). The Beckmann DU spectrophotometer is employed.

Iron. The spectrophotometric method of 1,10-phenantroline was utilized. By the end of 1977, we shifted to the ECSS norm (Doc. 118/76) which includes a bromine charge so as to cause the iron complete dissolution. The Beckman DU spectrophotometer is employed.

Zinc, chromium and nickel. Each one of these cations is also dosed in the same atomic absorption spectrophotometer with flame (AAS), according to techniques adopted by the

CRPQF Laboratory, based on the methods employed for the determination of the same cations, in brines.

To avoid burdening the text, the results obtained from statistic calculations are given in attached tables and the initial analytical data are collected in a special available report.

STATISTICAL TREATMENT OF DATA

Sea salt. The analytic results from the raw marine salt were taken in its totality (1970-1976) and calculated the respective mean, the standard deviation and the more probable medium value referred at reliable interval of 90% (Table 5).

We resorted to the normal reduced curve as selection criterion to eliminate outstanding values. In that sense, and considering the total of 209 samples, we worked with a reduced variable of 3.3. Then, there is a probability of $.4995 \times 2$ for the analytic outcome may be found in the interval $-3.3, +3.3$, which corresponds to a frequency of .209, to come to values superior to $\{3.3\}$.

After due elimination, the mean, the standard deviation and reliable interval of 90% were recalculated (Table 6).

After, took place the correction of that mean values in function of the tonnages corresponding to the various samples (Table 7).

Last, and from that data, a hypothetical medium composition is indicated (Table 8).

Rearrangement of data. On the other hand, we assorted the initial outcome according to salterns (producing regions) to compare them. We consider the salt of the first harvesting in 1972 from Aveiro, Figueira da Foz, Sado and Algarve salterns.

TABLE 5
Crude Salt (1970-1976)

	Loss of Mass (%)	Insoluble in Water (%)	Sodium Chloride (%)	Calcium (%)	Magnesium (%)	Sulphates (%)
N	209	209	209	209	209	209
S_x (%)	2.253	.321	2.342	.138	.503	1.265
\bar{x} (%)	6.532	.170	95.18	.186	.693	1.619
int. (90%)	$6.532 \pm .2563$	$.170 \pm .0364$	$95.18 \pm .2665$	$.186 \pm .0157$	$.693 \pm .05727$	$1.619 \pm .1843$

TABLE 6
Crude Salt (1970-1976)

	Loss of Mass (%)	Insoluble in Water (%)	Sodium Chloride (%)	Calcium (%)	Magnesium (%)	Sulphates (%)
N	208	190	203	198	206	194
S_x (%)	2.19	.083	1.805	.0621	.421	.6122
\bar{x} (%)	6.49	.095	95.44	.162	.660	1.331
int. (90%)	$6.49 \pm .249$	$.095 \pm .0097$	$95.44 \pm .2084$	$.162 \pm .00726$	$.660 \pm .0482$	$1.331 \pm .07230$

TABLE 7

Crude Salt

	S _x pop (%)				x pop (%)				int. (90%)			
	1971	1972	1975	1976	1971	1972	1975	1976	1971	1972	1975	1976
Loss of mass (%)	1.360	1.980	2.463	1.631	5.92	6.24	6.31	5.45	5.92 ± .743	6.24 ± 3.26	6.31 ± 4.10	5.45 ± .638
Insoluble in water (%)	.04713	.07572	.0605	.0585	1364	.08368	.0813	.101	.1364 ± .2576	.08368 ± .1262	.0813 ± .0996	.101 ± .0240
Sodium chloride (%)	1.293	1.802	1.3557	1.230	95.20	95.66	95.51	95.64	95.20 ± .7066	95.66 ± 2.964	95.51 ± 2.230	95.64 ± .4757
Calcium (%)	.0453	.0712	.0508	.0503	.107	.179	.159	.141	.197 ± .0247	.179 ± .117	.159 ± .0836	.141 ± .0195
Magnesium (%)	.219	.4318	.4519	.619	.590	.7476	.798	.383	.590 ± .120	.7476 ± .7103	.798 ± .743	.383 ± .124
Sulphates (%)	.5996	.5247	.7993	.488	1.567	1.335	1.563	.891	1.567 ± .3276	1.335 ± .8631	1.563 ± 1.315	.8915 ± .1885

TABLE 8

Hypothetical Composition of Crude Salt

	1971	1972	1975	1976
Sodium chloride	93.70	93.16	93.21	94.47
Calcium sulphate	.668	.608	.539	.478
Magnesium sulphate	1.38	1.14	1.48	.694
Magnesium chloride	1.225	2.030	1.955	.952

TABLE 9

Comparison of Different Salterns (Year: 1972; Harvesting: 1st)

Saltern	Number of Samples	Loss of Mass		Insoluble	
		\bar{x}	s^2/N	\bar{x}	s^2/N
Algarve	6	4.783	.1636	.07167	.00002944
Sado	6	6.933	.8144	.1667	.005478
Figueira da Foz	5	6.22	.1444	.148	.007804
Aveiro	6	7.3	.2907	.3617	.005029
		2.174		4.078	
		2.589		1.902	
		3.754		1.886	

$$t_{A-B} = (\bar{x}_A - \bar{x}_B) / \sqrt{\frac{S_A^2}{N_A} + \frac{S_B^2}{N_B}}$$

TABLE 10

Influence of the Harvesting Sequence on the Amount of NaCl and Mg⁺⁺ (Year: 1972)

	Number of Samples				Indicators		
	Algarve	Sado	Aveiro	Total	d(%)	s _d (%)	t
NaCl	2	6	7	15	1.44333	1.6638	3.29
Mg ⁺⁺	2	6	7	15	-.2913	.3979	2.835

From Tagus we were unable to dispose of samples which belong to the first harvesting.

To carry out the comparison, the mean, the variance and the *t* test were calculated (Table 9).

Next, the original data were collected according to the sequence of the harvesting (Table 10). In fact, in the small traditional saltworks are still carried out several partial harvestings every year.

TABLE 11
Contaminants in Crude Salt

Pb				Hg				Cu				Fe				Zn			
N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%
40	.13	.22	.22 ± .034	18	.00263	.00337	.00337 ± .00102	40	.280	.333	.333 ± .0727	*41	47.71	25.58	25.58 ± 12.26	36	1.45	1.50	1.50 ± .398
												24	4.87	10.30	10.30 ± 1.704				
												**17	69.37	47.18	47.18 ± 29.38				

*all determinations

** bromine oxidation method

TABLE 12
Contaminants per Salterns

	Pb			Hg			Cu			Fe			Zn		
	N	s _x ppm	\bar{x} ppm	N	s _x ppm	\bar{x} ppm	N	s _x ppm	\bar{x} ppm	N	s _x ppm	\bar{x} ppm	N	s _x ppm	\bar{x} ppm
Aveiro	7	.30	.31*	4	.0020	.0023	7	.076	.23	7	4.084	12.70	7	2.61	2.11
Fig. ^a da Foz	5	0	.20	—**	—	—	5	.045	.18	5	7.62	17	3	.902	2.07
Tejo	3	.058	.13	2	0	.001	3	.21	.43	1	—	9.4	3	.346	1.4
										2	8.77	***49			
Sado	3	0	.2	1	—	.0046	3	.17	.3	1	—	***35	3	1	1.6
										2	4.95	8.5			
Algarve	22	0	.2	11	.00288	.0041	22	.349	.391	14	5.281	9.414	20	1.11	1.20
										9	92.97	***64.89			

*86% of the results have a .2 ppm mean

**all the results are under .001 ppm.

***bromine oxidation method

TABLE 13

Contaminants of the Different Salterns (t test results)

Salterns	Pb	Hg	Cu	Fe	Zn
Sado-				.867*	
-Algarve	0	—	.729	.242	.633
				.965	
				1.13 *	
Tejo-Sado	2.00	—	.853	.257	.327
				2.26	
Figueira da Foz-				1.33 *	
-Tejo	2.00	—	2.08	2.23	1.201
				4.52	
Aveiro-	.999	—	1.39	1.15	.0427
-Figueira da Foz					

*all determinations

The mean and the standard deviation of contaminants were computed as was the probable medium values for reliable interval of 90% (Table 11). The same results were next grouped by salterns, and re-proceeded to a new statistical treatment (Table 12).

Then, we tried to compare the various salterns as to the contaminants values availing ourselves of the *t* test (Table 13).

Treated salts. Concerning the purified types, the results available were separated by producer plants. The means, the standard deviations and the limits are expressed in Table 14.

The limits on this Table refer to the percentages of samples within legal characteristics. The annual determination of general mean values were calculated (Table 15). The

limits shown, on this Table, are the major percentages of the general annual productions with good characteristics.

For that purpose, the annual production of each plant was considered as well as its analytical determinations. It was accounted the population mean, the variance of the population of means, and, finally, the population variance, followed by upper and lower limits (Table 15).

As to refined, table and iodized salt, the calculations carried out are expressed on Tables 16, 17 and 18.

The comparison between refined and table salt was made employing the *t* test (Table 19).

The comparison between iodized salt obtained from purified salt and the one coming from vacuum salt, carried out by the same test, may be seen on Tables 20 and 21.

These cations were tested in final purified salt as well as in the product taken immediately after each one of the technological operations.

However, not enough data is available for each producing unit, so we preferred not to do interplant comparisons. Thus, we only show the mean, standard deviation and medium value relative to a reliable interval of 90% for the total results obtained (Table 22).

For the refined and table salt, the statistical indicators are calculated relatively to iron, copper and lead (Tables 23 and 24).

Table 25 refers to the few data available for other contaminants.

TABLE 14
Purified Salt (1964–1976)

Plants	N	Loss of Mass			N	Insoluble in Water			N	Sodium Chloride		
		s_x (%)	\bar{x} (%)	upper limit (%)		s_x (%)	\bar{x} (%)	upper limit (%)		s_x (%)	\bar{x} (%)	lower limit (%)
A	56	.30	.68	89% \leq 1%	56	.111	.113	88% \leq .2%	56	.65	98.12	71% \geq 98%
B	7	.29	.41	100% $<$ 1%	7	.065	.073	86% $<$.2%	7	1.09	98.66	57% \geq 98%
C	24	2.0	1.4	75% \leq 1%	24	.029	.05	100% $<$.2%	24	1.1	97.54	58% \geq 98%
D	47	1.5	1.3	64% \leq 1%	47	.091	.07	89% $<$.2%	47	1.1	98.00	70% \geq 98%
E	25	.37	.83	68% \leq 1%	25	.349	.146	96% $<$.2%	25	1.2	97.67	56% \geq 98%
F	32	.23	.56	97% \leq 1%	32	.036	.051	100% $<$.2%	32	.64	98.14	75% \geq 98%
G	36	.33	.43	94% $<$ 1%	36	.053	.042	97% $<$.2%	36	.44	98.77	100% \geq 98%
H	27	1.3	1.0	78% $<$ 1%	27	.1	.090	100% $<$.2%	27	1.3	97.9	70% \geq 98%
I	26	.363	.78	77% \leq 1%	26	.067	.082	96% \leq .2%	26	.540	98.19	81% \geq 98%

TABLE 15
Purified Salt

Year	Loss of Mass			Insoluble in Water			Sodium Chloride		
	s_x pop (%)	\bar{x} pop (%)	upper limit	s_x pop (%)	\bar{x} pop (%)	upper limit	s_x pop (%)	\bar{x} pop (%)	lower limit
1972	.24	.67	80% \leq 1%	.027	.062	99% \leq .1%	.38	98.21	80% \geq 98%
1973	.11	.63	80% \leq .7%	.21	.20	80% \leq .15%	.31	98.22	85% \geq 98%
1974	.23	.55	99% \leq .95%	.030	.062	75% \leq .10%	.54	98.72	98% \geq 98%
1975	.19	.60	75% \leq .8%	.046	.072	75% \leq .08%	.20	98.27	90% \geq 98%
1976	.14	.36	98% \leq .6%	.048	.095	75% \leq .1%	.16	98.52	98% \geq 98%

TABLE 16
Refined Salt

Loss of Mass				Insoluble in Water				Chlorine & Chlorides				Calcium				Magnesium				Sulphates			
s_x	\bar{x}	int.		s_x	\bar{x}	int.		s_x	\bar{x}	int.		s_x	\bar{x}	int.		s_x	\bar{x}	int.		s_x	\bar{x}	int.	
N	%	%	90%	N	%	%	90%	N	%	%	90%	N	%	%	90%	N	%	%	90%	N	%	%	90%
20	.061	.029	.029 \pm .023	20	.011	.008	.008 \pm .0041	20	.23	60.33	69.33 \pm .0896	20	.004	.002	.002 \pm .0014	20	.020	.009	.009 \pm .0076	20	.079	.067	.067 \pm .031

TABLE 17

Table Salt

Loss of Mass				Insoluble in Water				Chlorine & Chlorides				Calcium				Magnesium				Sulphates			
N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.
%	%	%	90%	%	%	%	90%	%	%	%	90%	%	%	%	90%	%	%	%	90%	%	%	%	90%
26	.0672	.0569	.0569± .0225	26	.054	.018	.018± .018	26	.2055	60.07	60.07± .0688	26	.0015	.0039	.0039± .0017	26	.0412	.0162	.0162± .0138	26	.0494	.0473	.0473± .0165

TABLE 18

Iodized Salt

	Loss of Mass	Insoluble in Water	Chlorine and Chlorides	Potassium Iodide
N	12	12	12	12
S _x (%)	.0801	.102	.3822	2.899
\bar{x} (%)	.553	.515	98.47	16.68
int. (90%)	.553±.0416	.515±.0530	98.47±.1982	16.67±1.503

TABLE 19

Refined Table Salt Comparison (t test results)

Loss of Mass (100–110°C)	Insoluble in Water	Chlorine and Chlorides	Calcium	Magnesium	Sulphates	Iron	Copper	Lead
1.50	.891	3.52	1.85	.777	.95	4.17	.635	.192

TABLE 20

Iodized Salt

From:	Loss of Mass				Insoluble in Water				Sodium Chloride				Potassium Iodide			
	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.
		%	%	90%		%	%	90%		%	%	90%		%	%	90%
Purified Salt	8	.088	.58	.58± .059	8	.117	.523	.523± .782	8	.3964	98.35	98.35± .2656	8	2.208	17.50	17.50± 1.48
Vacuum Salt	4	0	.50	.50± 0	4	.0779	.50	.50± .0917	4	.2449	98.70	98.70± .2883	4	3.753	15.05	15.05± 4.418

TABLE 21

Purified-Iodized and Vacuum-Iodized Comparison
(t test results)

Loss of Mass	Insoluble in Water	Sodium Chloride	Potassium Iodide
2.59	.397	1.88	1.205

TABLE 22

Treated Salt Contaminants

Pb				Hg				Cu				Fe				Zn			
N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.	N	s _x	\bar{x}	int.
ppm	ppm	ppm	90%	ppm	ppm	ppm	90%	ppm	ppm	ppm	90%	ppm	ppm	ppm	90%	ppm	ppm	ppm	90%
33	0	.20	.20± 0	13	.0024	.0028	.0028± .0012	27	.185	.289	.289± .0608	33	7.14	14.3	14.3± .286	22	1.35	1.18	1.18± .463
												*18 4.07 18.7 18.7± 1.67							
												15 6.46 8.99 8.99± 4.09							

*Bromine oxidation method

TABLE 23

Refined Salt Contaminants

Fe				Cu				Pb			
N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%
19	.5025	.2842	.2842 ± .1999	20	.1721	.0860	.0860 ± .0665	19	1.1350	.4579	.4579 ± .4515

TABLE 24

Table Salt Contaminants

Fe				Cu				Pb			
N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%	N	s _x ppm	\bar{x} ppm	int. 90%
25	2.3941	2.3360	2.3360± .8193	26	.1023	.0585	.0585± .0343	21	1.0747	.3905	.3905± .4045

TABLE 25

Other Contaminants in Refined and Table Salts

	Hg ppb	Zn ppm	Cr ppm	Ni ppm
Refined Salt	<0.2	0.4–0.5	<0.4	<0.4
Table Salt	<0.2	0.4–0.5	<0.4	<0.4

RESULTS

Raw salt. The elimination of the statistically outstanding values brought out the following values decreases (see Tables 5 and 6):

Loss of mass	.042%
Insolubles	.075%
Calcium	.024%
Magnesium	.033%
Sulphates	.29 %

and an increase of:

Sodium chloride	.26 %
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The number of results discarded and its percentages, referred to a total of 209 samples are given below:

Loss of mass	1 (.5%)
Insolubles	19 (9.1%)
Sodium chloride	6 (2.8%)
Calcium	11 (5.3%)
Magnesium	3 (1.4%)
Sulphates	15 (7.1%)

The numeric limits adopted for the exclusions were, respectively:

Loss of mass	≥	14.6 %
Insolubles	≥	.38%
Sodium chloride	≤	82.8 %
Calcium	≥	.38%
Magnesium	≥	2.46%
Sulphates	≥	3.6 %

Table 8 shows great amounts of magnesium chlorides and sulphates and low amounts of sodium chlorides due to two principal reasons, the salt considered was never washed and the major number of samples came from small traditional saltworks, where technology is more adequate to get good organoleptic characteristics than chemical ones.

Comparison among salterns. We verified that concerning sodium chloride, calcium magnesium and sulphate tenors, no differentiation was noted among the several salterns, but Table 9 shows that Aveiro and Algarve are outstanding, respectively, as to insolubles and loss of mass.

The first region has a probability greater than 90%, a greater value as to insolubles, because of a special kind of sand used to compact the crystallizers bottoms.

Algarve, with the same probability, shows a lower loss of mass, due to the relative advanced technology, as well as to the better climatic conditions.

Comparison among harvestings. Concerning the sodium chloride and magnesium tenors, Table 10 allows one to differentiate the first from the second extractions. While the first suffers a drop (99% of probability), the second rises (98% of probability). The difference is due to the absence of drainage of residual brines, in traditional salt ponds. No statistical differences were detected between the second and the third harvestings.

Contaminants. Table 11 shows that lead presents a medium tenor of .22 ppm relative to a total of 40 samples analyzed. 92.5% of the results are of .2 ppm and 5% of .1 ppm. For mercury, for a total of 41 determinations, there were 21 less than .001 ppm, i.e., 51.2% of the total, and 2 less than .0001 ppm (4.9%).

In other 18 samples, the average tenor was of .0034 ppm (43.9%) being the minimum value .001 ppm and the maximum .0076 ppm.

Copper shows a medium value rather high, .33 ppm, being 10% of the results of .1 ppm and 37.5% of .2 ppm. We notice that these results are from a non-washed salt.

Iron, in 24 samples shows a value of 10.30 ppm, varying between 2 ppm and 17.5 ppm. In another 17 samples the mean was 47.18 ppm with limits of 11 ppm and 300 ppm.

The last group of determinations was according to the bromine oxidation method. Zinc shows a 1.5 ppm mean and rather heterogeneous values. Table 12 shows the medium values for different regions and Table 13 the results of the *t* test among salts of various origins. The geographic variation is probably caused by differentiated brines, soils, equipments and technologies.

Treated salts (purified salt). The considerable heterogeneity of the products coming from different plants may be observed in Table 14 and it suggests a big variation of equipment and technological operations.

The general evolution of the medium characteristics during the period considered may be seen on Table 15.

The loss of mass drop, detected in 1976, is eventually due to technical development, chiefly in the drying sector, as well as to the modernization of the supplying saltworks themselves. The values shown on Table 14 are different from corresponding ones of Table 15, because they are taken from different years.

Calcium, magnesium and sulphate cake are not shown. In this type of salt and in intermediate treatment phases, the few available results are not enough to reach to conclusions.

Contaminants are shown in Table 22. It denotes that among the contaminants found in purified salt and in its intermediate products, lead is the one whose value is more uniform (.2 ppm). Mercury's low medium value is remarkable and in 13 determinations slightly less (.0028 ppm) than the one observed in crude salt (.0034 ppm). 30% of samples had a value less than .0001 ppm and 27% less to .001 ppm.

Copper shows a medium value of .289 ppm, which is rather high, although, a somewhat inferior to the raw salt one.

From a first lot of 15 results, iron shows a medium concentration of 8.99 ppm, varying from 3.8 to 23.8 ppm. A second lot of 18 samples shows a mean of 18.7, varying from 12.0 to 26.0 ppm. The last one was processed according to the bromine oxidation method. Zinc, with a medium of 1.18 ppm suggests a certain irregularity.

Refined salt. Table 16 shows that the product is in accord with the legislation referred above. The medium values are even considerably less than the legal limits.

Contaminants values are also below the legal limits, especially for copper (.086 ppm), lead (.46 ppm) and iron (.28 ppm) (Table 23). The few existent results concerning other contaminants seem to be low (Table 25).

Table salt. For this type, the conclusions are similar to those for the refined salt, but the value for halogens is very close to the legal limit. Table 19 proves that these two kinds of salt are identical, except for halogens and iron.

Iodized salt. Table 18 indicates that this type has characteristics similar to purified salt regarding loss of mass and sodium chloride, but differing as to insolubles in water. This one is not comparable to those for purified salt, due to the presence of tricalcic phosphate utilized as stabilizer additive (4.98 g/kg). The heterogeneity of the potassium iodide is probably due to variable permanency time in the warehouses.

Table 21 confirms that the iodized salt coming from purified or vacuum ones has dissimilar chemical characteristics.

FINAL SYNTHESIS

Incomplete aspects of this paper are observed in some aspects, principally, from the reduced number of available samples. On the other hand, at this evolutionary stage of the salt industry in Portugal it is not possible to specialize a characterization of its product.

In fact, there are still traditional technologies which are disappearing so modern ones can start. It will be more important later to compare the data collected here with future ones.

In any case, the convenience of accelerating the technical development in course is shown. So, the progressive requirements of the consumers will be better satisfied.