

# CHANGE IN THE METHOD FOR SALT ANALYSIS IN JAPAN

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## 1. Introduction

The analysis method in quality inspection should be simple, preserving the environment, and accurate. Japan had been under the Salt Monopoly System from 1905 to 1997<sup>1)</sup>, and the Method for Salt Analysis was published as JMC's Salt Analyzing methods in 1907<sup>2)</sup>. Now, it has been revised as "Methods of analysis for salt", which have been widely used by researchers and analysts in the salt industry.

In the past 100 years, there have been drastic improvements in analytical instruments, and accordingly, the analysis methods have changed in a variety of ways. In this report, we will describe the transitions of the methods for salt analysis in Japan and the development status of the analytical technique we have been engaged in.

## 2. Outline of the salt inspection method

The salt inspection method employs an indirect analysis process to measure chloride, primary impurities (magnesium, calcium, potassium, sulfuric acid ion), insoluble matter, loss of drying, and transformed into sodium chloride (see table 1). Using this method, sodium chloride is calculated as bound in the form of molecules<sup>3)</sup>; sulfuric acid is calculated as a calcium sulfate and the remnant calcium is regarded as calcium chloride. When the amount of sulfuric acid ion is greater than required to bind calcium into calcium sulfate, the excess will be bound into magnesium sulfate, and if sulfuric acid ion still remains, it will be regarded as sodium sulfate. The remnant magnesium will be regarded as magnesium chloride. Potassium is regarded as potassium chloride, and the remnant chloride will be calculated as sodium chloride.

However, for high purity salt, a simple analysis method to calculate chloride by deducting impurities can also be employed.

## 2.1 Halogens

It is important to analyze halogens in the analysis of salt. The silver nitrate titration method (Mohr's method) is generally used, and in the Method for Salt Analysis, has been employed since its initial publication 100 years ago. Another method is mercurimetry; in the Codex Alimentarius commission, the analysis method for measurement of chloride in food grade salt was discussed, and mercurimetry was adopted in 1982<sup>4,5)</sup>.

Additionally, ASTM is a well-known standard too, the analytical standard of sodium chloride

is provided. A comparison of method of analysis for sodium chloride and ASTM E534<sup>6)</sup> is shown in Table 1 (in ASTM534 a simple analysis method is employed as for the above-mentioned high purity salt).

Nino et al. compared mercurimetry with the silver nitrate titration method in accuracy, time required and expense, and reported that their accuracy and reproducibility were at the same level. As for the time required, it was reported that the silver nitrate titration method required 20 minutes while the mercurimetry required 25 minutes, and the former was found to be more cost-effective<sup>7)</sup>.

Table 1 Method of analysis for Sodium Chloride

Content	Japan -1907	Japan -1961	SICJ* -2002	Codex** ISO and ECSS	ASTM E534
Loss on drying	Gravimetry 135-140°C,	Gravimetry 140°C, 90min.	Gravimetry 140°C, 90min.	Gravimetry 110°C, Constant	Gravimetry 110°C,
Insoluble matter	Gravimetry 100-105°C	Gravimetry 110°C, 60min.	Gravimetry 110°C, 60min. glass filter	Gravimetry 110°C, 60min. glass filter	Gravimetry 110°C, 60min.
Halogens	Argentometry 0.1M AgNO <sub>3</sub>	Argentometry 0.04M AgNO <sub>3</sub>	Argentometry 0.1M AgNO <sub>3</sub>	Mercurimetry 0.1M Hg(NO <sub>3</sub> ) <sub>2</sub>	none
Sulfate	Gravimetry BaSO <sub>4</sub>	same as left	Ion Chromatography	Gravimetry BaSO <sub>4</sub>	Gravimetry BaSO <sub>4</sub>
Calcium	Gravimetry CaCO <sub>3</sub>	Titration KMnO <sub>4</sub>	ICP-OES & Titration EDTA	Titration EDTA	Titration EDTA
Magnesium	Gravimetry Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Titration H <sub>2</sub> SO <sub>4</sub>	ICP-OES & Titration EDTA	Titration EDTA	Titration EDTA
Potassium	Gravimetry K <sub>2</sub> [PtCl <sub>6</sub> ]	Titration KMnO <sub>4</sub>	Volumetry & Flame	Volumetry & Flame photometry	none
Sodium chloride	Calculation	Calculation	Calculation	Calculation	100 % - impurities <sup>***</sup>

\*SICJ; The Salt Industry Center of Japan (Japan Monopoly Co. was predecessor concern of SICJ.)

\*\*CODEX; according to ISO exclude potassium. Potassium is according to ECSS (European Committee for the Study of Salt)

\*\*\* Impurities; Sum of loss on drying, Insoluble matter, Sulfate, Calcium and Magnesium



Figure 1 shows the "z score" in the analysis evaluation examination that we have been carrying out. Though overseas analysts are also participating in this examination, two-thirds of the participants are Japanese analysts using the silver nitrate titration

method; therefore, we cannot make a simple comparison, but we consider that the analytical value in mercurimetry shows the same accuracy as that in the silver nitrate titration method.

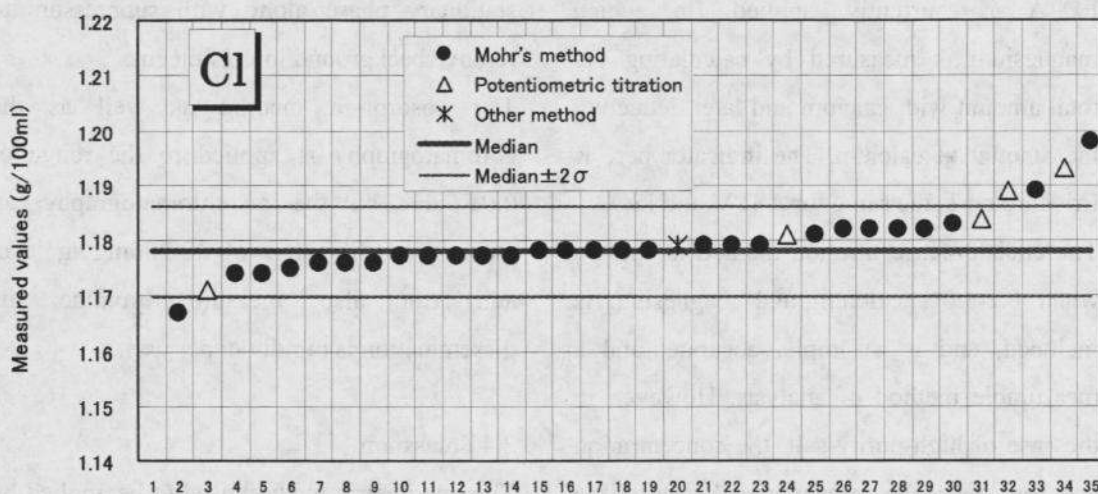


Fig. 1 z-score graph at measured halogens in analysis performance assessment scheme by SICJ

Another analysis method is the constant-current titration method. The advantages of this method are that it allows automation and does not use potassium chromate as the indicator. On the other hand, its equipment is expensive and can produce errors according to the composition of the sample, which have prevented us from adopting the method. However, as for no use of the potassium chromate, it becomes easy to process the waste liquid and the quality of analysis equipment has increased by means of technological advancement, we are planning to consider the possibility of its introduction.

## 2.2 Calcium and Magnesium

Gravimetric method was applied as an analysis method of the calcium before. This

method is for creating calcium oxalate deposition by using oxalic acid, changing it into calcium carbonate in weak heating, and measuring its weight. This method was thereafter developed into the oxidation titration method in which calcium oxalate is changed into permanganate. Chelatometric titration by using disodium ethylenediamine tetraacetate dehydrate (EDTA) is currently utilized, and it is simple as well as having improved the efficiency. In the salt inspection method

2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (HSNN) is used as an indicator, whereas ASTM uses ammonium purpurate (murexide) and ISO uses glyoxal-bis-(2-hydroxyanil), GBHA<sup>8)</sup>.

The weight of magnesium was measured by

causing it to precipitate as magnesium ammonium phosphate before. The substance was changed into the sulfuric acid titration method thereafter, but this method exhibited defects in its rapidity and accuracy. Therefore, the chelatometric titration method by using EDTA is currently applied, in which magnesium is measured by calculating the total amount with calcium and later deducting the amount of calcium. The indicator here is Eriochrome T, the same for ASTM and ISO.

The chelatometric titration method is applied when 0.2-1.0% calcium and magnesium is included, and is a simple, accurate, and a measurable method of analysis. However, in the case of high-purity salt, the concentration was too low to be measurable; therefore, the inductively coupled plasma optical emission spectrometry (ICP-OES) instrumental analysis method has come into use. Our institute applies the chelatometric titration and the ICP-OES analysis depending on the concentration range. Recently, since ICP-OES with a multi-type optical isolation system has become widely used enabling the simultaneous measurement of multiple elements. We are planning to consider the possibility of the simultaneous measurement method including minute impurities.

### 2.3 Sulfuric acid ion

Sulfuric acid ion used to be measured with gravimetry by creating a barium sulfate deposition<sup>9)</sup>; ISO<sup>10)</sup> and ASTM still employs this method. In the present salt inspection method, the chromic acid ion eluted in liquid is measured with a spectrophotometer by adding the suspended chromic acid barium to a sample solution, causing the sulfuric acid to

precipitate. More recently, this method is being substituted for the ion chromatography. This method is utilized to measure the single component separated in the ion chromatography by placing ion exchange columns with a weak ionic resins in a stationary phase along with suppressors to remove background ions of eluent.

The absorption method as well as the chromatography is applied to the range of 0.01-0.4%, but the ion chromatography can measure in the range of 20-200mg/kg level and can also measure bromide, its dissemination is rapidly under way.

### 2.4 Potassium

The gravimetric method used to be applied by using tetra phenyl sodium borate and other substances, but recently potassium is measured using the flame photometry or the atomic absorption spectrometry except that the gravimetric method is applied to a salt containing potassium chloride abundantly. The application concentration density ranges for each method are 0.01-0.3% for the flame photometry, and 10-250mg/kg for the gravimetric method. In many foreign countries, potassium is not measured, and in ASTM, potassium is regarded as a trace component and not measured, either.

### 2.5 Loss of drying

Loss of drying is originally an index representing water; in ASTM, the heating temperature is 110°C (120 minutes), and in ISO, the heating temperature is also 110°C (until it becomes a constant mass)<sup>11)</sup>. However, since most of the salt sold in Japan contains impurities from seawater, magnesium chloride



hydrate and other salts hydrates, the hydrated water cannot be measured under such temperature conditions. Therefore, in the salt inspection method, the heating temperature is 140°C (120 minutes) when considering these hydrated salts<sup>12)</sup>, and the provided numerical value is represented as heating weight loss. Moreover, concerning salts with high water content and many impurities, the revised burning weight loss occurs at 600°C for 90 minutes as well as causing the change of magnesium chloride into magnesium oxide<sup>13)</sup>.

## 2.6 Insoluble matter

In the salt inspection, salt samples are solved in water and filtered with a glass fiber filter with a pore diameter of 1 micro meter, and the residual materials on the filter will be measured. ASTM and ISO<sup>14)</sup> use similar kinds of filters, but their pore diameters are indicated as 0.3 micro meters, 4-16 micro meters

respectively.

## 3. Minute impurities

In the salt test method, the analysis methods of copper, lead, zinc, iron, manganese, chrome, vanadium, arsenic, strontium, nickel, cadmium, mercury and aluminum are prescribed. Most of these elements are analyzed with the ICP-OES method because of no requirement in preprocessing operations including desalinations of the measurement sample and enabled high-sensitivity analyses. We have shown the detection concentration ranges of various elements in figure 2.

We are currently developing a high-accuracy ICP-MS method to separate the target element only through preprocessing purposes using a heated disk or an ion chromatography. We expect that the method would be utilized as an analysis method for individual existing of heavy metals and other materials.

H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg											
Lantanoid		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
Actinoid		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					
H	0.1% over																				
F	1-1000 mg/kg																				
Ca	1-1000 μg/kg																				
Be	1-1000 ng/kg																				

Fig. 2 Concentration range of detectable in salt

#### 4. Additives

Recently in Japan, an edible salt including various additives is sold in the market, and the analysis method for additives is being developed accordingly. In the past several years, the analysis method for citric acid and malic acid<sup>15)</sup>, and the ferrocyanide used as an anti-blocking agent<sup>16)</sup>.

#### 5. Safety remarks

Our center has been engaged in the observance of domestic safety standards as well as international standards that Japan has ratified. The safety standard of edible salt published by Codex includes the concentration standard for copper, lead, cadmium, and arsenic, and by using the abovementioned minute component analysis method, we use to periodically validate that these elements have satisfied the reference values.

The Japanese Ministry of the Environment prescribes the salt as an anti-freezing agent with an environmental standard. This standard is applied for such elements as cadmium, lead, chrome, arsenic, mercury, copper and selenium, as well as organic compounds including Polychlorobiphenyls (PCBs), organic phosphorus, and agricultural chemicals and so on (See Table 2). The methods of analysis of these compounds are developed, and it can satisfy the demand of

such an analysis now, too.

The Japanese Ministry of Health, Labor and Welfare enforces regulations for the residue-prone agricultural chemicals in food ("Positive list"), and our center verifies that agricultural chemicals have not been contaminated into the manufacturing process. We have developed and have been adopting new methods mainly utilizing gas chromatography / mass spectrometry and liquid chromatography / mass spectrometry<sup>17)</sup>.

Another criteria is a production standard that our center had originally established, which confirms that the production process from raw material (seawater) to the product. As for seawater, in addition to the observance of the aforementioned environmental standards enforced by the Ministry of the Environment, we monitor the dissolution components from the apparatus and material balance of food additives in the salt manufacturing process, and to confirm whether marine bacteria and the extreme halophile remain in the process as a sanitary supervision, we are regularly investigating the process survey. The methods of analysis have been established about a necessary analytical method for verifying the safety of the process.



Table 2 Environmental Quality Standards for soil pollution in Japan

Substance	Target level of soil quality examined through leaching and content		
cadmium	0.01 mg/L or less	dichloromethane	0.02 mg/L or less
total cyanide	not detectable	carbon tetrachloride	0.002 mg/L or less
lead	0.01 mg/L or less	1,2-dichloroethane	0.004 mg/L or less
chromium (VI)	0.05 mg/L or less	1,1-dichloroethylene	0.02 mg/L or less
arsenic	0.01 mg/L or less	cis-1,2-dichloroethylene	0.04 mg/L or less
total mercury	0.0005 mg/L or less	1,1,1-trichloroethane	1 mg/L or less
alkyl mercury	not detectable	1,1,2-trichloroethane	0.006 mg/L or less
copper	less than 125 mg/kg	trichloroethylene	0.03 mg/L or less
selenium	0.01 mg/L or less	tetrachloroethylene	0.01 mg/L or less
benzene	0.01 mg/L or less	1,3-dichloropropene	0.002 mg/L or less
organic phosphorus	not detectable	thiuram	0.006 mg/L or less
PCBs	not detectable	simazine	0.003 mg/L or less
		thiobencarb	0.02 mg/L or less

## 6. Conclusion

We have studied and developed an analytical technology that can be applied to quality inspections. Based on these efforts, we have now acquired ISO 17025, an international authentication, as an examination organization and engage in the entrusted analyses of various salt samples. We will achieve the simplification and the efficiency improvement of the analysis operation and development of new analytical techniques according to the demands and the changes in the society in the future.

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