AN APPROACH ON THE METHOD OF DETERMINATION OF POTASSIUM FEROCYANIDE IN EDIBLE SALT

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Disputes always exist on the determination of potassium ferrocyanide in solar salt and no suitable solution has been found. We all know that no potassium ferrocyanide is added as anti-caking agent during the production process of solar salt and no potassium ferrocyanide is produced from the raw sea water and its production process. However, 1~4mg/kg of potassium ferrocyanide is detected as per the standard determination method. Such a result complies with the requirement specified in the State Standard <Edible Salt>. But problems will occur when products pickled with such salt are marked with no detected potassium ferrocyanid for export or are to be applied for green food. The users use solar salt for pickling purpose while no addition of potassium ferrocyanide is verified with the determination report by the legal testing organ. The result of determination shows the existence of potassium ferrocyanide due to the problem of determination method. Why does this result happen?

The relevant testing organs are ceaselessly looking for the solution. China National Sea Salt and Lake Salt Standardization Center and China National Well and Rock Salt Standardization Center revised the standard for determination of potassium ferrocyanide in the year of 2003. Pyridine-pyrazolone method is included in the standard for the detection of potassium ferrocyanide in edible salt and the determination of trace potassium ferrocyanide. Since then, several determinations have been conducted with pyridine-pyrazolone method by our Center with no potassium ferrocyanide detected. However, the actual operation of this method is too complicated with more reagents, longer time and higher cost. The former ferrous sulfate method is easier, quicker and less costing. The fact is that the determination of potassium ferrocyanide in edible salt conducted in other industries rather than salt industry is ferrous sulfate method.

1. THEORETICAL APPROACH

According to theoretical analysis, the principle of ferrous sulfate method is based on the fact that the reaction of potassium ferrocyanide with ferrous sulfate under acidic condition produces white precipitant of ferrous ferrocyanide which becomes Prussian blue when oxidized by air. Its concentration is determined with ultraviolet spectrophotometry. According to the principle of Lambert-Beer's Law, under given conditions (i.e. the fixed monochromatic light wave length, fixed solvent, fixed temperature and the same size of cell, etc.), the absorptance of uniform and non-scattering solution is linearly related to its concentration. It is true that there are many factors affecting Lambert-Beer's Law, such as chemical factor and optical factor. The existence of positive deviation is due to the existence of colloid and suspended matter in the solution that makes the higher absorptance because of light scattering. Hence higher concentration is detected. Scattering is caused by the scattering function of the particle on the light pass. Scattering is different from reflection and refraction, which scatters to all directions in the space and reduces transmission light. For the true solution, the scattering light is not so powerful because of

small particles. In the same time, it does not affect the absorptance because of blank comparison. However, some impure solutions which contain macromolecules such as colloid and protein can drastically increase the scattering. And blank comparison is not easy to prepare for such solutions. Therefore, the absorptance determined may be higher and the concentration detected may be higher, too.

2. PROOF TEST

Based on this scattering phenomenon, the author filtered different samples of edible salt in order to reduce the impact of macromolecules on the absorptance during test and to understand the impact of impure samples on the test result. Samples were dissolved in proper amount of distilled water and filtered with ashless paper. Comparison was made with the solution that was not filtered. Treatment was made in accordance with the ferrous sulfate method specified in the standard GB/T13205.10-2003. Absorptance was determined and comparison test of potassium ferrocyanide content was conducted. The results are as follows:

Table 1 Results of Determination of Potassium Ferrocyanide in Different Solutions (mg/kg)

Type of Salt	Solar Salt (without anti-caking agent)			Crushed salt (without anti-caking agent)		Refined Crushed Salt (with anti-caking agent)	Gourmet Powder Salt (without anti-caking agent)	Refined Salt (with anti-caking agent)
Place	Zhoushan	Putuo	Ningbo	Shandong (0512)	Shandong (0602)	Hubei	Meishan	Hubei
Not Filtered	2.7	3.4	1.6	5.1	4.4	13.1	0	4.2
Filtered	0	0	0	0	0	12.7	0	3.5

Table 2 Result of Determination in Bottom Solution After Settling (mg/kg)

Type of Salt	Solar Salt		Crushed Salt	
Not Filtered	3.7	4.0	9.5	7.5
Filtered	0	0	0	0

Data in Table 1 fully indicates that obvious difference exists between the filtered and the not filtered solutions of solar salt and crushed salt. However, there is no obvious change, or almost the same for refined salt. Refined salt is recrystallized with brine that is made by dissolving raw salt. During dissolving process, impurities are removed with chemical treatment. Solar salt is made in open air by natural evaporation and crystallization. Many impurities are included. Impurities in crushed salt, though washed, still remain, even higher than solar salt. Therefore, crushed salt is the impurest and refined salt is the cleanest with solar salt in the middle in terms of insoluble matters and suspended matters. This can easily interpret why the test results of crushed salt solution and solar salt solution which are not filtered are higher in view of the scattering phenomenon of the solution. Data in Table 2 also indicates the existence of scattering phenomenon. For solar salt, there are less precipitates. And for crushed salt, there are more precipitates. Therefore, the tests show that there is almost no change between solar salt and supernatant solution and that there is more difference for crushed salt.

The results of recovery rate in Tables 3 and 4 indicate that the recovery rate of solar

salt solution that is not filtered is unstable and low, failing to meet the requirement for analysis. However, the recovery rate of filtered solar salt solution is stabilizes at ≧ 95%, meeting the requirement for trace analysis.

Table 3 Results of Recovery Rate Test of Solar Salt (mg/kg)

Standard Solution of $[Fe(CN)_6]^{4-}$ Added(ug)	0	10	20	30
Not Filtered	1.6	3.5	5.0	7.1
Filtered	0	1.9	3.8	5.9

Table 4 Results of Recovery Rate (%)

Standard Solution of $[Fe(CN)_6]^{4-}$ Added(ug)	0	10	20	30
Not Filtered	——	95.0	85.0	91.7
Filtered	——	95.0	95.0	98.3

3. CONCLUSION

It is concluded from what has been discussed above that the solution samples have to be pre-treated when determining the potassium ferrocyanide content in salt with ferrous sulfate method, especially the solar salt and crushed salt solutions that contain more impurities. Pre-treatment is a must whether the solution looks turbid or not. Solar salt solution does not look turbid sometimes. It is true that some suspended matters and organic substances are clung to it during the production process, which can not be found by eye. The result of test will be higher if no treatment is made. The above-mentioned solutions are not turbid. No treatment is needed if test is carried out in accordance with the standard GB/T13025.10-2003<The General Testing Method for Salt Industry—Determination of Potassium Ferrocyanide>. However, the results are quite different as compared with the filtered solution. Therefore, it is recommended that the filtering process be written in this standard when it is revised so as to enhance the correctness of the method.

References

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