



NOTE

Simultaneous Determination of Iodide, Sulphate, Fluoride and Nitrite in Salt Samples by Ion Chromatography

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Simultaneous determination of iodide, sulphate, fluoride and nitrite in salt samples by ion chromatography was demonstrated in this paper. To avoid the interference of Cl^- , solid Ag_2O was used as a precipitator. After that, ascorbic acid was added to reduce the iodate to iodide ion. In the analysis process, IonPac-RAS19 4×250 mm was selected with IonPacAG19 4×50 mm as guard column. Leachate of potassium oxide solution was used with 1 mL/min flow velocity. Linearity ranges of iodide, sulphate, fluoride and nitrite were 0.1-10, 0.05-1, 0.01-0.80 and 0.01-0.80 $\mu\text{g/mL}$, respectively and high correlations (R^2) were all above 0.999. Limits of detection (LOD) were 10 mg/kg (iodide ion), 5 mg/kg (sulphate), 1 mg/kg (fluoride) and 1 mg/kg (nitrite). This method is simple and convenient with rapid, accurate and high sensitivity which could be accepted in daily analysis.

Keywords: Ion chromatography, Table salt, Iodide, Fluoride, Sulphate, Nitrite.

Iodine is usually added in salt to prevention the iodine deficiency disease worldwide. Therefore, the treated salt was called iodide salt. Low or high inputs of iodine could both bring the negative impacts on human health¹. The sulphate, fluoride and nitrite in salt samples were generally regarded as impurities. Higher concentrations of them indicate lower salt purity. In analysis of iodine, more attention should be paid to the influence of large amount of chloride ion, which could cause heavy disturbance². At present, silver-column method is always used to remove chloride ion in other negative ion determination with ion chromatography methods for its highest efficiency^{3,4}. But it is expensive for large amount of silver would be used in the process of high levels of chloride ion solution passing through the high capacity Ag^+ -exchange column. So the silver-column method is not widely accepted for expensive cost. Then the solid Ag_2O was selected to remove chloride ion in this study. Now, the determination methods of iodine in salt sample are mainly focus on volumetric method, catalytic dynamics method and gas chromatographic method⁵⁻⁸. In addition, spectrophotometric method has been used to analysis of sulphate, fluoride and nitrite⁹⁻¹¹, while the process is termwise with large workload for a long period and even the data results are always influenced by the experimental conditions and manual operation. Electrical conductivity detector of ion chromatography could simultaneously determination of iodide, sulphate, fluoride and nitrite in salt samples. This

method is simple operation, rapid, accurate and could meet requirements in daily analysis.

ICS-2000 instrument equipped with automatically generator of eluent was used in the experiment. Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA) and used to confect all standard solutions. Standard solutions of potassium iodate, sulphate, fluoride and nitrite were all purchased from National Research Center for Certified Reference Material (NRCCRM) of China.

Anion analytical column (Dionex IonPac AS19, 4×250 mm), guard column (Dionex IonPac AG19, 4×50 mm), suppressor (ASRS 4 mm), electrical conductivity detector, leaching with 30 mmol/L KOH at a flow rate of 1 mL/min, suppression current was 75 mA and injection volume was 25 μL , the column temperature was 30 °C.

Sample pretreatment: About 1 g salt sample and 0.10 g ascorbic acid were weighted and mixed in volumetric flask. After dissolution, about 15 mL solution were taken out and injected in 20 mL centrifuge tube. After added 0.3 g Ag_2O , the black Ag_2O turned into white AgCl precipitate with continuous agitation by glass rod. More Ag_2O was added up to the black precipitate occurred, which indicated the excessive Ag_2O existing in solution. Centrifuged for 2 min, 10 mL supernatant were taken out and put them pass through 0.22 μm membrane filter. Leachate was used to determination.

TABLE-1
PRECISION AND RECOVERY STUDIES (n = 6)

Parameters	Concentration ($\mu\text{g/mL}$)	Amount recovered ($\mu\text{g/mL}$)	Recovery (%)	RSD (%)
I^-	0.20	0.21	105.0	3.25
	3.00	3.09	103.0	2.30
	5.00	4.99	99.8	1.07
SO_4^{2-}	0.20	0.19	95.0	2.77
	0.50	0.51	102.0	1.45
	1.00	1.01	101.0	1.10
F^-	0.20	0.19	95.0	3.56
	0.40	0.41	102.5	2.31
	0.80	0.79	98.7	1.50
NO_2^-	0.20	0.21	105.0	3.03
	0.40	0.39	97.5	2.46
	0.80	0.83	103.7	1.79

'n' is number of determinations and RSD is relative standard deviation

Reductant selection: Ion chromatography method to determination of iodine had been reported¹² and always the iodine in salt was directly determined in those methods. But now, the salt sold in the market is always added with potassium iodate¹³, it is necessary to reduce the iodate to iodide for more accurate results. Various reducing agents, such as hydrazine hydrate, hydroquinone, sodium thiosulfate, sodium sulphide and ascorbic acid were tested in our experiments. Among them, neither hydrazine hydrate nor hydroquinone is suitable for the required reduction condition. The effects of thiosulfate, sodium sulphide and ascorbic acid behaved better. But considerate of the high affinity ability of thiosulfate to anion exchange column, which meant longer analysis time and lower working efficiency, the thiosulfate was not the first choice. Sodium sulphide, as another reducing agent, large amount of them would influence the detection of iodide anion¹⁴. Ascorbic acid had no above faults and was suitable to all the required conditions. In this paper, the effects of five levels of ascorbic acid (0.1, 0.5, 1.0, 5.0 and 10 %) were attempted. When the concentration of 0.1 % was tested, the iodate could be turned into iodide completely. Therefore, this is the suitable concentration of ascorbic acid.

Added amount of Ag_2O and stirring time: The colour of precipitate was used to control the amount of Ag_2O . When less Ag_2O added, the black Ag_2O would be turned into white AgCl . With more Ag_2O added, the colour of solution will become black, which indicated excessive Ag_2O existing in solution. After stirring for 8 min, the reducing velocity of Cl^- was very slow. At this time, the Cl^- could not influence the detection of other anions and no stirring needed any more. The time of 8 min was selected as stirring time.

Linear range and limit of detection: The linear ranges of iodide ion, sulphate, fluoride and nitrite in salt samples were 0.1-10.00, 0.05-1.00, 0.01-0.80 and 0.01-0.80 $\mu\text{g/mL}$, respectively. The calibration curves of the target substances showed good linearity with $R^2 > 0.999$. The limit of detection was estimated at a S/N of 3 and the results were 10 mg/kg (iodide ion), 5 mg/kg (sulphate), 1 mg/kg (fluoride) and 1 mg/kg (nitrite).

Degree of precision and accuracy: Standard solutions were added in the salt samples with known concentrations. With low, middle and high levels of standard solutions added and analyzed for 6 time, the RSD (relative standard deviation) could be calculated as 1.30-3.25 % (iodide ion), 1.10-2.77 % (sulphate), 1.50-3.56 % (fluoride), 1.79-3.03 % (nitrite). The recovery of them

were 99.8-105, 95-102, 95-102.5 and 97.5-105 %, respectively. The results could be accepted (Table-1).

Effect of co-existing ion: As demonstrated in Fig. 1, after separated by ion separation column, the common anion like as Cl^- , NO_3^- , PO_4^{3-} could be separated completely and no interference happened.

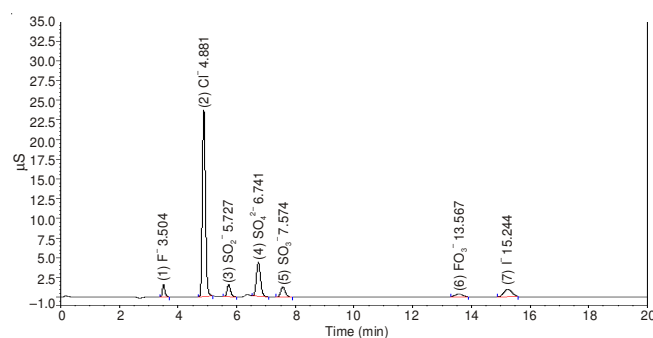


Fig. 1. Chromatogram of salt sample without chloride ion

The results of degree of precision indicated the method built in the experiment was suitable to simultaneously determination of iodide ion, sulphate, fluoride and nitrite in salt samples. Compared to other methods, this method has high sensitivity, good selectivity, simple operation, less disturbance and lower cost. It could be accepted in simultaneously determination of iodide, sulphate, fluoride and nitrite in salt samples in daily analysis.

REFERENCES

1. Y. Zhao and X.-Y. Lin, *Chin. J. Publ. Health*, **22**, 492 (2006).
2. People's Republic of China National Standard, Hygienic Standard for Food Grade Salt, (GB 2721-2003).
3. P. Razpotnik, J. Turšič, M. Veber and M. Novic, *J. Chromatogr. A*, **991**, 23 (2003).
4. L. Barron and B. Paull, *Anal. Chim. Acta*, **522**, 153 (2004).
5. G.-R. Mo, *Chin. J. Nat. Med.*, **4**, 149 (2007).
6. H.-Q. Huang, *Food Sci.*, **23**, 122 (2002).
7. H.-T. Fu, *Chinese J. Anal. Chem.*, **31**, 376 (2003).
8. L. Zhu, *Chinese J. Health Lab. Technol.*, **15**, 1334 (2005).
9. S.-M. Mo and L.-N. Liang, *Fenxi Ceshi Xuebao*, **25**, 105 (2006).
10. People's Republic of China National Standard, Physical Part of Food Hygiene Inspection (GB/T5009.42-2003).
11. People's Republic of China National Standard, Physical Part of Food Hygiene Inspection (GB/T5009.33-2010).
12. R.D. Rocklin and E.L. Johnson, *Anal. Chem.*, **55**, 4 (1983).
13. Y.-L. Yang and L. Lin, *Chinese J. Anal. Chem.*, **38**, 1381 (2010).
14. H.-T. Fu, L.-M. Fu and Y.-L. Zhang, *Chinese J. Anal. Chem.*, **27**, 684 (1999).