Na Analysis by Atomic Absorption

■ Introduction

The sodium's crustal abundance is the 6th largest following the elements oxygen, silicon, aluminum, iron and calcium, and it exists mainly in such forms as rock salt (NaCl), Chile saltpeter ($NaNO_3$) and natural soda (Na_2CO_3). Furthermore, the salt content in seawater is about 34g/L, and after the chlorine ion, the sodium ion is present in the next highest quantity at about 11g/L.
Metallic sodium is obtained from electrolysis of a salt solution mixture of sodium chloride (NaCl) and calcium chloride. Sodium is an extremely soft metal having a silver color, and after silver, copper and gold, has great electrical conductivity. In addition, sodium is highly reactive, reacting violently with water to generate heat and hydrogen gas, and produce sodium hydroxide (NaOH). When heated in air above its melting point, it ignites and is converted to the light-yellow colored sodium peroxide (Na_2O_2). Under high temperature and high pressure, it further reacts to form white colored superoxide (NaO_2).
Sodium possesses a strong reducing characteristic, and this is utilized to produce margarine by adding hydrogen to the carbon double bond in vegetable oil. Further, it has a low melting point allowing its easy conversion to the liquid state, and with its high heat conductivity and other characteristics, it is used as a coolant for removing heat from nuclear reactor.
Various useful salts can be made from sodium. For example, sodium hydroxide is used in such chemical industrial fields as paper and pulp, soap, etc. In the case of sodium hydroxide, since it is deliquescent, allowing it easily absorb moisture, it must be handled with care. Sodium bicarbonate ($NaHCO_3$) is used for such products as neutralizing agents and stomach antacids as well as baking soda and baking powder, etc. Sodium chloride, beyond its use as a seasoning, is used as a raw material for producing sodium hydroxide, sodium carbonate as well as metallic sodium.
Concerning sodium in living organisms, potassium is present in greater quantities in plants than sodium, however, in animals, sodium exists in greater quantities. In humans, sodium is present at about the rate of 1.5g/kg, and of that, 0.9g/100mL is present in blood, in which it plays roles in maintaining the shape of red blood cells and maintaining intracellular ion balance.
Analysis of sodium is conducted for environmental applications as well as nutrition- related applications for the food industry. Further, because sodium is so prevalent in the environment, it is widely analyzed as an index of environmental pollution in the semiconductor and electronic materials fields.

■ Basic Data of Na

Atomic mass	: 22.99
Melting point	: 97.8˚C
	(NaCl : 800.4˚C ; $NaNO_3$: 308˚C)
Boiling point	: 882.9˚C
	(NaCl : 1413˚C ; Na_2SO_4 : 1429˚C)
Oxidation number	: −1 : Ex. Metallic sodium in liquid ammonia
	+1 : Ex. NaOH, Na_2CO_3, Na_2O,
	+2 : Ex. NaO
Solubility	: NaCl 35.8g/100g water(20˚C)
	$NaNO_3$ 91.8g/100g water(25˚C)

Reference : Physics and Chemistry Dictionary, etc.

■ Sodium Measurement Wavelengths

	Sensitivity Ratio
589.0nm	1.0
589.6nm	0.48
330.3nm	0.002

■ Flame Analysis of Na

In analysis of samples such as foods which contain large amounts of sodium in the form of salts, dilution is indispensable. However, since increasing the dilution factor is accompanied by a greater risk of dilution error and contamination, instead of dilution, it is also possible to perform measurement at a lower instrument sensitivity as a countermeasure. In flame analysis, sensitivity adjustment by the simple method is available, in which the burner angle is changed. By adjusting the angle, the optical path length is changed, thereby changing the sensitivity accordingly. When using the 10cm burner, when the angle is changed to 90˚ the sensitivity becomes 1/20th of that at 0˚. This corresponds to the ratio of the optical path length of 10cm at 0˚ and flame thickness of 5mm at 90˚.
One thing to consider when performing analysis of sodium by the flame method is the addition of acid to the measurement solution. While no acid is added to the 1000ppm sodium standard solution itself, it is indispensable to add acid to the measurement solution. In analysis of basic metals such as sodium and potassium, if measurement is conducted without adding acid, there are such tendencies as the calibration curve at low concentrations becoming raised at the bottom, and yielding lower sensitivity as compared to when acid is added. These phenomena are mainly due to ionization interference, however, they can be inhibited by the addition of acid.
Since the sodium analysis line resides at longer wavelengths than that covered by the D2 lamp wavelength region (190 – 430nm), the D2 lamp cannot be used for background correction. Normally, since there is rarely a problem with background in the long wavelength region, measurement can be conducted without correction. However, in cases where the background in this region cannot be ignored, an effective correction method is the SR (Self Reversal) method. Fig. 1 and 2 show a profile and calibration curve, respectively, without background correction, and Fig. 3 and 4, using the SR method.

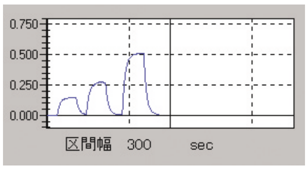

Fig. 1 Profile without Background Correction

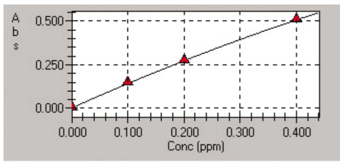

Fig. 2 Calibration Curve without Background Correction

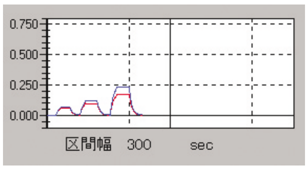

Fig. 3 Profile using SR Method

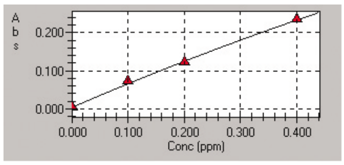

Fig. 4 Calibration Curve using SR Method

■ Furnace Analysis of Na

Since sodium is an element that is easily contaminated and at the same time has extremely high sensitivity, when performing measurement at the highest sensitivity, sodium is often detected from the blank. This problem is resolved by using Ar gas flow during atomization to enable measurement at the lower sensitivity. In the Furnace method, techniques used aside from this one to decrease sensitivity include changing the analysis wavelength, decreasing the sample injection volume, etc.

Examples showing a comparison of sensitivity at 589.0nm and 589.6nm are shown in Fig. 5, 6, 7 and 8. The sample injection volume was 10µL, and the heating conditions under which measurements were conducted are shown in Table 1. A platform tube was used for the graphite cuvette. To decrease the sensitivity, Ar gas flow at 0.2L/min was used during atomization for all the measurements.

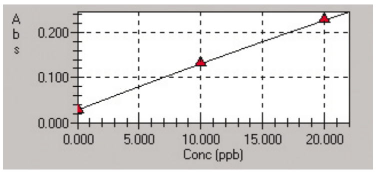

Fig. 7 Calibration Curve of Na (589.0nm)

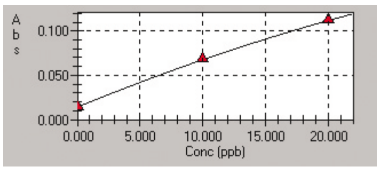

Fig. 8 Calibration Curve of Na (589.6nm)

Table 1 Heating Conditions

	Temp.	Heating Time	Heating Method	Ar Flow Rate
1	250	20	RAMP	0.1
2	250	10	RAMP	0.1
3	800	10	RAMP	1.0
4	800	10	STEP	1.0
5	1800	3	STEP	0.2
6	2500	2	STEP	1.0

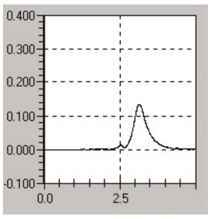

Fig. 5 Profile using Furnace Method (589.0nm)

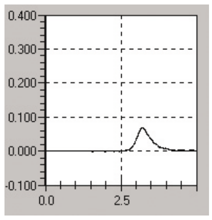

Fig. 6 Profile using Furnace Method (589.6nm)

■ Conclusion

When performing atomic absorption analysis, regardless of the analysis element, it is necessary to adequately consider interfering substances in the matrix. With sodium, which belongs to the group of basic metals having low ionization electrical potential, ionization interference is a problem in flame measurement. In particular, when there is a large amount of easily ionized metals coexisting in the sample matrix, a marked degree of interference can be seen. To curb this ionization interference, it is effective to add the same amount of easily ionized elements to both the standard solution and the sample. Potassium or cesium are often used as interference inhibitors.

In furnace measurement, the presence of the chloride ion in the sample is the primary factor in the formation of chloride compounds. In general, since chlorides have a low melting point and are easily volatilized, chloride formation is the cause of decreased sensitivity and reproducibility. For that reason, nitric acid is used more often than hydrochloric acid in preparing solutions for furnace analysis. In the case of sodium, however, since the melting point of the chloride is higher than that of nitrate, it can be said that addition of the chloride is more effective than that of the nitrate from the viewpoint of inhibiting volatility. On the other hand, when performing analysis of an element where NaCl becomes the interfering component, nitric acid converts the NaCl to $NaNO_3$, and is sometimes added with the aim of enhancing volatilization during ashing, so it can also be said that nitric acid can be used as an interference inhibitor.

Sodium, comprising about 2.63% of the earth's crust and about 0.63% of soil, can be said to be a ready source of contamination from the environment. In such fields as the electronic and semiconductor fields, it is used as an index of pollution along with such elements calcium and zinc. With this in mind, it is necessary to be aware of and take the necessary measures with respect to contamination from the environment, tools and reagents when conducting ultra trace analysis of sodium.

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