The Determination of Sodium, Calcium and Silicon in Pure Water by Graphite Furnace AA

Application Note

Atomic Absorption

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Introduction

In the production of integrated electronic chips, a very important process is to rinse with pure water. If trace elements were to remain on the chips, short circuits could occur between the high density components.

The presence of the elements calcium, sodium, iron and silicon in the process rinse water causes the most difficulties. The ubiquitous nature of these elements means that they are likely and dangerous contaminants. Therefore the levels of these elements in the process rinse water must be monitored continuously and routinely.

As the levels of calcium, sodium, iron and silicon in the process rinse water must be low, it is necessary to achieve good sensitivity and high reproducibility. This requirement indicates that graphite furnace atomization is the most suitable technique.

Experimental

An Agilent SpectrAA-30A atomic absorption spectrometer with a GTA-96 graphite tube atomizer and PSD-96 programmable sample dispenser was used. Agilent hollow cathode lamps were used. Argon (99.999%) was used as the inert gas.

Water was deionised by using a Servo Mischbettfilter ionic exchange filter (Hager and Elsasser, Stuttgart) and then polished using a Nanopure Reinstwasseranlage D-1797 (Wilhelm Werner, Bergisch-Gladbach). The analytical conditions for sodium, calcium and silicon are summarized in Table 1.

Table 1. Analytical Conditions for Sodium, Calcium and Silicon

	Na	Ca	Si
Instrument mode	Absorbance	Absorbance	Absorbance
Calibration mode	Concentration	Concentration	Concentration
Measurement mode	Peak height	Peak height	Peak height
Lamp current (mA)	5	10	20
Slit width (nm)	0.5	0.5	0.2
Slit height	Reduced	Reduced	Reduced
Wavelength (nm)	589.0	422.7	251.6
Sample introduction	Sampler automixing	Sample automixing	Sample automixing
Replicates	5	5	5
Background correction	Off	Off	Off

A furnace temperature program was developed for each element. A concentration calibration graph for each element was obtained using the automatic dispensing features of the PSD-96. The instrument parameters are summarized in Table 2 (sodium), Table 3 (calcium) and Table 4 (silicon). The stock calibration concentrations (placed in the Standard/ Reslope position) were:

Na	1 ng/mL
Ca	5 ng/mL
Si	100 ng/mL

For calcium, 0.5% v/v nitric acid was used as a chemical modifier.

Table 2. Ca Pure Water

Furnace parameters

Step no.	Temperature (C)	Time (sec)	Gas flow (L/min)	Gas type	Read command
1	90	2.0	3.0	Normal	No
2	120	30.0	3.0	Normal	No
3	400	1.0	3.0	Normal	No
4	1200	2.0	3.0	Normal	No
5	1200	2.0	3.0	Normal	No
6	1200	2.0	0.0	Normal	No
7	2600	0.7	0.0	Normal	Yes
8	2600	2.0	0.0	Normal	Yes
9	2700	0.1	3.0	Normal	No
10	2700	2.0	3.0	Normal	No
11	90	13.1	3.0	Normal	No

Sampler parameters

	Solution (µL)	Blank (µL)	Modifier (µL)
Blank	—	20	5
Standard 1	4	16	5
Standard 2	8	12	5
Standard 3	12	8	5
Standard 4	16	4	5
Standard 5	20		5
Sample	20		5

Recalibration rate	0
Reslope rate	0
Multiple inject	No
Hot inject	No
Pre inject	No

Table 3. Na Pure Water

Furnace parameters

Step no.	Temperature (C)	Time (Sec)	Gas flow (L/Min)	Gas type	Read command
1	90	2.0	3.0	Normal	No
2	120	30.0	3.0	Normal	No
3	300	1.0	3.0	Normal	No
4	700	2.0	3.0	Normal	No
5	700	2.0	3.0	Normal	No
6	700	2.0	0.0	Normal	No
7	2000	0.7	0.0	Normal	Yes
8	2000	2.0	0.0	Normal	Yes
9	2600	0.3	3.0	Normal	No
10	2600	2.0	3.0	Normal	No
11	90	12.7	3.0	Normal	No

Sampler parameters

	Solution (µL)	Blank (µL)	Modifier (µL)
Blank	—	20	
Standard 1	5	15	
Standard 2	10	10	
Standard 3	15	5	
Standard 4	20		
Sample	20		

Recalibration rate	0
Reslope rate	0
Multiple inject	No
Hot inject	No
Pre inject	No

Table 4. Si Pure Water

Furnace parameters

Step no.	Temperature (C)	Time (Sec)	Gas type (L/Min)	Gas flow	Read command
1	90	2.0	3.0	Normal	No
2	120	35.0	3.0	Normal	No
3	900	2.0	3.0	Normal	No
4	900	2.0	3.0	Normal	No
5	2600	0.9	0.0	Normal	Yes
6	2600	2.0	0.0	Normal	Yes
7	2700	0.1	3.0	Normal	No
8	2700	1.0	3.0	Normal	No
9	90	13.1	3.0	Normal	No

Sampler parameters

	Solution (µL)	Blank (µL)	Modifier (µL)
Blank	—	25	
Standard 1	5	20	
Standard 2	10	15	
Standard 3	15	10	
Standard 4	25		
Sample	25		

Recalibration rate	0
Reslope rate	0
Multiple inject	No
Hot inject	No
Pre inject	No

Results and Discussion

The Blank

Normally the blank and standards are made up in ultrapure water. When ultrapure water itself is being analyzed, this causes some practical difficulties. For this study, no liquid was injected for the blank measurement. The standards would potentially have systematic errors because of the unknown amounts of the analytes in the ultrapure water itself. However, the results indicate that these levels are very low. Five replicate readings were measured for each solution.

The calibration graph for calcium (Figure 1) was linear with a correlation coefficient calculated to be 0.997 (Table 5). The samples analyzed were in the range 0.5 to 4.0 ng/mL (Table 6).

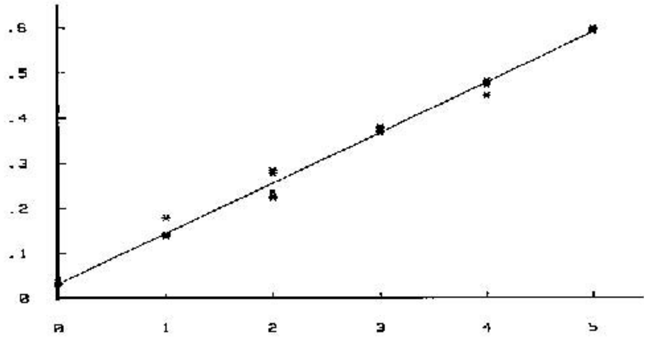

Figure 1. Calibration graph for calcium in ultrapure water.

Table 5. Process Characteristics for the Detection of Na and Ca in Pure Water (DIN 38 402)

	Detection	Determination	Correlation	RSD	t-value 99.9
Na	0.05	0.08	0.996	0.006	3.849
Ca	0.20	0.31	0.997	0.025	3.725

Table 6. Ca Analyses of Deionized Water (VE water) and Pure Water (Five Replicates)

Sample	Concentration (ng/mL)	RSD%	Mean absorbance
VE-water I	1.380	1.9	0.153
Pure water I	0.858	1.9	0.097
VE-water II	2.065	1.2	0.222
Pure water II	0.946	5.4	0.107
VE-water III	3.087	2.7	0.346
Pure water III	2.172	3.5	0.235

The calibration graph (Figure 2) for sodium was also linear and the correlation coefficient was calculated to be 0.996 (Table 5). Signal graphics are shown in Figure 3. The samples analyzed were in the range 0.2 to 0.7 ng/mL with the RSD between 2% and 9%. The calibration graph for silicon (Figure 4) was not linear. A polynomial line of best fit is shown in Figure 5. The samples analyzed had no detectable silicon.

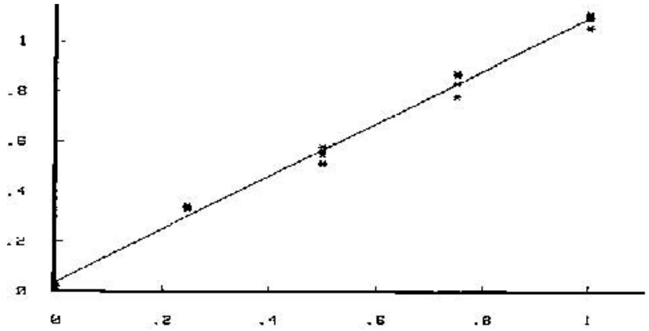

Figure 2. Calibration graph for sodium in ultrapure water.

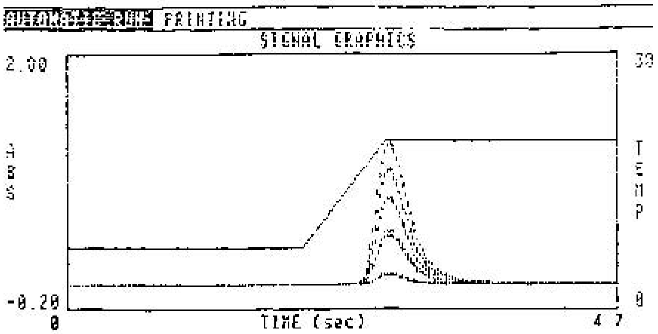

Figure 3. Overlay of sodium signals for the calibration graph.

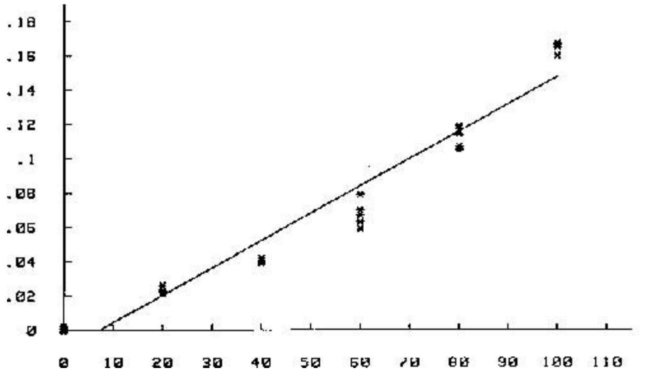

Figure 4. Calibration graph for silicon in ultrpure water, linear fit.

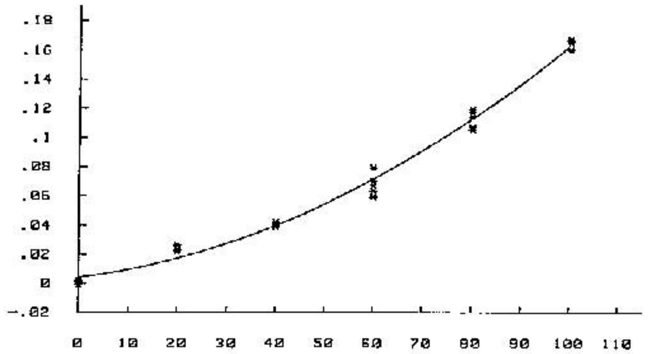

Figure 5. Calbibration graph for silicon in ultrapure water, 2nd order polynomial curve fit.

Detection Limit

Detection limit can be calculated by two methods, IUPAC and DIN 38 402. The detection limit calculated using the IUPAC definition for each of the three elements is summarized in Table 7. The DIN definition could be used to calculate detection limits for sodium and calcium. The detection limits and other calculated values are summarized in Table 8. The DIN definition could not be applied to silicon because of its non-linear calibration graph.

Table 7. Multiple Injection with Ca Solutions of 0.4 ng/mL (Sample A) and 2 ng/mL (Sample B)

	Absorbance X	**Concentration Ca (ng/mL)**	**RSD % N=5**	**For X5 concent'n theoretical value (ng/mL)**
Sample A 1 injection	0.049	0.4	6.2	1.96
Sample A 5 injections	0.252	2.0	7.3	
Sample B 1 injection	0.263 2	2.1	4.6	

Table 8. Detection Limit for Na, Ca and Si, Calculated After the IUPAC Definition

	Na	**Ca**	**Si**
Detection limit (ng/mL)	0.06	0.13	2.1

Multiple Injection

The GTA-96 and PSD-96 can be programmed to do multiple injections. The sample is injected and the furnace cycle continues as normal to step 2 (Table 4) to dry the sample. This can be done for up to 99 injections. After the last sample is injected, the furnace program completes the full cycle. Calcium was studied this way. A 0.4 ng Ca/mL solution was single injected and multiple injected five times and compared with a single injection of a 2.0 ng Ca/mL solution. It would be expected that the lower concentration solution injected five times should be identical to the higher concentration solution injected once. Table 8 shows that the concentrations and absorbances compare very well. Multiple injections of sodium and silicon showed similar results. Hence, detection limits for each element could be improved by a factor of 10 to 20.

Conclusion

The levels of calcium, sodium and silicon in ultrapure rinse water can be determined using the parameters listed. The IUPAC detection limit for sodium was 0.06 ng/ mL, for calcium 0.13 ng/mL and for silicon 2.1 ng/mL. The DIN 38 402 detection limit for sodium was 0.05 ng/mL and for calcium 0.20 ng/mL. The use of multiple injection would allow an improvement in detection limit of a factor of 10 to 20.

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