

# ULTRASENSITIVE DETERMINATION OF SILICATE IN PROCESS AND BOILER WATER USING RAPID PHOTOMETRIC TESTS

Economic efficiency is becoming an ever more important aspect of everyday life, with the efficiency of industrial plants and equipment constituting one of the basic preconditions for sustainable economic operations. One avoidable problem that can result in losses of efficiency is posed by the undesirable build-up of deposits, i.e., scale – in pipes, boilers, and turbines.

A principal cause of scale in such equipment is silicate. Especially at high pressures – as in high-pressure turbines – silicate is deposited on the internal surfaces. This problem occurs mainly as a result of silicate dissolved in the steam.<sup>1</sup>

The expansion of the steam results in a reduction of the solubility capacity of silicate, which in turn leads to the formation of solid silicon dioxide on the surrounding surfaces, for example the turbine blades, reducing the efficiency of the plant.<sup>2</sup>

One measure that can help to minimise the need for time-consuming cleaning operations that interrupt the operation of the machine is to regularly inspect the boiler and boiler feed water for their silicate concentrations.

The guidance values depend on a variety of operating conditions (e.g., steam capacity, heating-surface load, and working pressure) of the boiler. In high-pressure turbines, even the slightest concentration of silicate in the steam can lead to deposits. To avoid such deposits, in most cases it is recommended to prevent steam silicate concentrations from exceeding 20 µg/L SiO<sub>2</sub>.<sup>3,4</sup> Depending on the operating conditions, the limit for silicate may even be as low as 10 µg/L SiO<sub>2</sub> or less.<sup>2</sup>

## Analytical Methods

The determination of concentrations of silicate in such a low range requires an extremely sensitive detection method. Graphite furnace atomic absorption spectrometry (GF-AAS) is frequently the method of choice here, capable of detecting concentrations of silicate down into the lower ppb range. Besides the element-analytical methods, classic photometry has also proven to be a reliable method.

This method is based on the reaction of silicate ions in acidic solution with molybdate ions to produce yellow silicomolybdic acid. The addition of a suitable reduction agent then produces deep blue silicomolybdenum blue, which is subsequently determined photometrically.<sup>5</sup>

## Silicate Test Kit

The molybdenum blue method is also the principle used in the photometric silicate test (Cat. No. 101813) of our Spectroquant® test kit series.

The advantage of this test is that it is quick and easy to use without major instrument investment needed. All necessary reagents are supplied in the test kit in a ready-to-use format. Compared with classic photometry, the use of the corresponding Spectroquant® photometers enables the time-consuming calibration procedure to be dispensed with, since the method is already pre-programmed into the devices. Using the 100-mm

cell, the Prove 600 spectrophotometer is capable of measuring silicate concentrations as low as 0.25 µg/L SiO<sub>2</sub>, thus ensuring the detection of extremely low amounts of dissolved silicate. The overall measuring range of the test kit is 0.25–500.0 µg/L SiO<sub>2</sub>.



Figure 1. Spectroquant® Prove 600 photometer

## Performance of the Measurement with Spectroquant® Silicate Test

The silicate content of process-water samples lies within the lower part of the measuring range of the test kit. During the course of the experiments it was found that the precision in the lower part of the measuring range can be enhanced when reagents Si-1 and Si-2 are added with a pipette instead of dropwise.

The procedure for the tests was correspondingly adapted. Moreover, the procedure described in the instruction sheet enclosed with the product has been changed from dropping

to pipetting to ensure the highest possible accuracy. Care was also taken to ensure that no glass equipment was used during the entire procedure. In the event of any turbidity of the sample solution, this must be filtered beforehand.

The silicate test starts by pipetting 20 mL of sample solution into a plastic test vessel, after which 200 µL of reagent Si-1 is added. The solution is mixed and then left to stand for 5 minutes. After the standing time, 200 µL reagent Si-2 is added and the solution mixed, then 1.00 mL of reagent Si-3 is added. The solution is mixed once again, left to react for 5 minutes, and then measured in the photometer against a reagent blank prepared with Ultrapure water in an analogous manner.

A detailed description of the procedure is described in the application "Ultrasensitive determination of silicate in process and boiler water". The application can be found online on the product page for Spectroquant® Silicate Test 101813.

## Standard Addition with Spectroquant® Silicate Test

In an experiment to gain an expressive statement on the suitability of the Spectroquant® Silicate Test for the determination of the silicate content in process water, the standard addition method was applied to five samples. Each sample was spiked with three different concentrations of silicate. In order to determine the recovered silicate concentration, the silicate concentration of the sample, also gained using the Silicate Test, was subtracted from the measured result of the spiked sample. For evaluation, the deviation of the recovered concentration from the target value (spiked concentration) was calculated. The results are shown in Table 1.

Table 1: Recovered content of silicate

Sample	Addition [µg/L SiO <sub>2</sub> ]	Recovered concentration [µg/L SiO <sub>2</sub> ]	Deviation [µg/L SiO <sub>2</sub> ]
Ultrapure water	1.00	0.86	0.14
	5.00	6.25	1.25
	10.00	10.60	0.60
Steam water from power plant	1.00	1.83	0.83
	5.00	6.14	1.14
	10.00	11.01	1.01
Boiler water from power plant	1.00	1.24	0.24
	5.00	6.09	1.09
	10.00	10.20	0.20
DI water	1.00	1.97	0.97
	5.00	5.74	0.74
	10.00	11.31	1.31
Double-distilled water	1.00	1.75	0.75
	5.00	7.40	2.40
	10.00	11.53	1.53

The recovered silicate spikes all lie within the 95% confidence value of 3.33  $\mu\text{g/L SiO}_2$ . The value of the deviation from the respective spike lies between 0.14 and 2.40  $\mu\text{g/L SiO}_2$ , averaging out at 0.93  $\mu\text{g/L SiO}_2$ .

The accuracy of the pre-programmed method is sufficient for many users. Users for whom the error rate of the pre-programmed method is still too large can, however, enhance the accuracy of the method by plotting their own custom calibration curve, thus eliminating batch-specific fluctuations and the user's own systematic errors.

A calibration curve was plotted for the Spectroquant® Silicate Test for the measurement range 0.50–25.00  $\mu\text{g/L SiO}_2$ , see Figure 2.

In the case of the silicate test, the custom calibration curve was able to improve the performance characteristics obtained acc. to ISO 8466-1, respectively DIN 38402 A51. A comparison of the performance characteristics of the pre-programmed method vs. the custom calibration is presented in Table 2.

At a value of 1.44%, the method coefficient of variation is 2.5 times higher than that of the pre-programmed method. This can be attributed to the fact that deviations have, in relative terms, a stronger effect in the lower measurement range as a result of the custom calibration. Seen in absolute terms, the custom calibration procedure can, however, result in considerably lower method errors, as shown by the values of the standard deviation for the procedure and the confidence interval. The method standard deviation and the confidence interval for P=95 % of the custom calibration are 76% (standard deviation) and 86% (confidence interval) lower than those for the pre-programmed method.

When the standard additions are evaluated using the user-specific calibration function, the deviations can be reduced down to the expected values. On average, the value of the deviation was now 0.29  $\mu\text{g/L}$ , indicating a reduction from the original value of 0.94  $\mu\text{g/L}$  by almost 70%. The measurement values are presented in Table 3.

## Method Comparison of GF-AAS and Spectroquant® Silicate Test

Besides the standard addition experiments, a reference analysis was also performed: the silicate content of the five water samples was quantified by a GF-AAS method. The Limit Of Quantitation (LOQ) of the GF-AAS method was determined using the ten-fold standard deviation of the blank, yielding a value of 1.93  $\mu\text{g/L SiO}_2$ . Table 4 compares the results from the GF-AAS method with those of the photometric determination method, calculated using the pre-programmed method and the custom calibration.

For three of the samples, the silicate concentration measured by the GF-AAS method lay below the LOQ of 1.93  $\mu\text{g/L SiO}_2$ , a finding that could also be confirmed by the measurement with the Spectroquant® test kit.

The power plant samples lay above the LOQ and the results of the GF-AAS method are comparable with those of the Spectroquant® test kit. The deviations are all within the 95% confidence interval of the pre-programmed method and that of the custom calibration (see Table 2). As was also the case for the standard addition, it is apparent that a custom calibration can serve to reduce the error even further.

## Summary

The above results show that the Spectroquant® Silicate Test is capable of yielding quantitative values for silicate concentrations in process water and deionized water in the lower ppb range. Users for whom the accuracy of the test for the determination of silicate is sufficient can use the pre-programmed method to determine the silicate content of their samples swiftly and effortlessly. In the event that greater accuracy of the method is required, the creation of the user's own custom calibration curve is recommended, which was shown to be capable of reducing the mean deviation of the spike amounts that were added by almost 70%.

## Instruments Used

All measurements were carried out as per the application on a Prove 600 spectrophotometer. The reference method that was

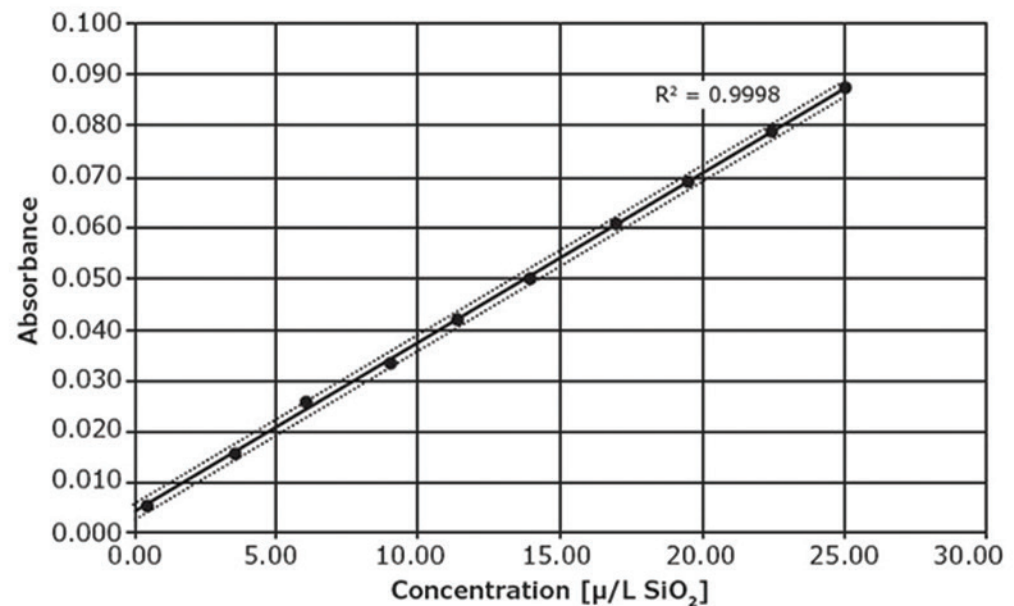


Figure 2: Calibration curve of Spectroquant® Silicate Test 101813, measuring range 0.50–25.00  $\mu\text{g/L SiO}_2$

Table 2: Comparison of performance characteristics

Sample	Addition [ $\mu\text{g/L SiO}_2$ ]	Recovered concentration [ $\mu\text{g/L SiO}_2$ ]	Deviation [ $\mu\text{g/L SiO}_2$ ]
Ultrapure water	1.00	0.70	0.30
	5.00	4.83	0.17
	10.00	10.28	0.28
Steam water from power plant	1.00	1.15	0.15
	5.00	5.42	0.42
	10.00	10.13	0.13
Boiler water from power plant	1.00	1.00	0.00
	5.00	5.12	0.12
	10.00	9.54	0.46
DI water	1.00	1.15	0.15
	5.00	4.97	0.03
	10.00	10.28	0.28
Double-distilled water	1.00	0.85	0.15
	5.00	6.45	1.45
	10.00	10.57	0.57

Table 3: Recovered contents of silicate, evaluated against the custom calibration

	re-programmed method 0.25 – 250.00 $\mu\text{g/L SiO}_2$	Custom calibration 0.50 – 25.00 $\mu\text{g/L SiO}_2$
Method standard deviation [ $\mu\text{g/L}$ ]	$\pm 0.790$	$\pm 0.185$
Method coefficient of variation [%]	$\pm 0.62$	$\pm 1.44$
Confidence interval (P=95 %) [ $\mu\text{g/L}$ ]	$\pm 3.33$	$\pm 0.45$

Table 4: Comparison of the results of the Spectroquant® Silicate Test 101813 and the GF-AAS reference analysis

Sample	Concentration [ $\mu\text{g/L SiO}_2$ ] Spectroquant® Silicate Test		
	GF-AAS	Pre-programmed method	Custom calibration
Ultrapure water	< 1.93	< 0.25	< 0.25
Steam water from power plant	2.25	3.26	2.18
Boiler water from power plant	3.66	4.85	3.94
DI water	< 1.93	0.29	< 0.25
Double-distilled water	< 1.93	0.77	< 0.25

used was a graphite furnace atomic absorption spectroscopy method on the SpectraAA 280Z instrument supplied by Agilent.

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