Application Note

October 28, 2020

Keywords or phrases:
Groundwater, filtration, dissolved heavy metals, ICP-MS, ICP-OES, throughput, extractables, recovery

In-line Filtration of Groundwater Samples for Heavy Metal Analysis with Sartolab® P20 Plus

Klaus Schöne[1,*], Kristin Menzel[2,*] and Catherine Leluan[1]

1. Sartorius Lab Instruments GmbH & Co.KG, Otto-Brenner-Str. 20, 37079 Göttingen, Germany
2. Validation Services Confidence®, Sartorius Stedim Biotech GmbH, August-Spindler-Straße 11, 37079 Göttingen

* Correspondence
E-Mail: klaus.schoene@sartorius.com, kristin.menzel@sartorius.com

Abstract

Filter membranes with a pore size of 0.45 µm are used for in-field sample preparation to investigate groundwater for dissolved heavy metals. Depending on the sample volume and the particulate load of suspended matter, so-called in-line filters can significantly streamline the sampling process, in contrast to the use of syringe filters. The Sartolab® P20 Plus in-line filter presented in this paper was compared with syringe filters with regard to its suitability based on throughput and particle reduction. As a result, we could show that Sartolab® P20 Plus filters are clearly superior to syringe filters in terms of throughput and particle reduction. Additionally, Sartolab® P20 Plus filters were tested for the release of heavy metals and their recovery after addition in several concentrations. Sartolab® P20 Plus do not release or adsorb any amounts of heavy metals relevant for groundwater monitoring. Based on the results, Sartolab® P20 Plus in-line filters are suitable for sample preparation of groundwater for heavy metal analysis and therefore significantly simplify on-site sampling.

Introduction

Filtration of groundwater is an essential step in the sampling procedure of dissolved heavy metals intended for further analysis, e.g., by ICP-MS or ICP-OES. With this straightforward approach, dissolved heavy metals can pass through the filter while the undissolved heavy metals, often associated with humic matter, are physically retained. For this separation step, filter membranes are used with a pore size of 0.45 µm when water is monitored in the context of official regulations.

Differentiation between dissolved and undissolved heavy metals for the determination of water quality is based on the correlation that aquatic organisms primarily resorb heavy metals in their dissolved form and that, among other factors, bioavailability and toxicity increase, depending on the concentration of the dissolved elements[1]. As a result, the European Groundwater Directive states that member states must control the chemical quality of groundwater, in particular the heavy metals arsenic, cadmium, lead and mercury[2]. Associated threshold values are defined by the individual member states, such as in the Groundwater Ordinance (GrwV) of Germany[3]. This Ordinance also recommends analysis of these four elements by membrane filtration using a 0.45 µm filter. Similar monitoring programs exist in the United States, and the U.S. Environmental Protection Agency (EPA) provides operating procedures for groundwater sampling in which filtered and non-filtered samples are utilized for elemental analysis.

During sampling, the water from a well is usually pumped to the surface using a submersible pump and tubing. The water can then be piped into a vessel from which a sample is taken and filtered using a syringe filter. Another way is to attach an in-line filter to the tubing and filter the water sample directly (Figure 1). Users report that, in a head-to-head comparison of the two methods, sampling using the Sartolab® P20 Plus in-line filter (Figure 2) is five times more effective in terms of throughput and filtration time, without compromising the quality of the sample, than the procedure using a syringe filter.

Fig. 2: Sartolab® P20 Plus in-line filter.

Heavy Metal Sampling

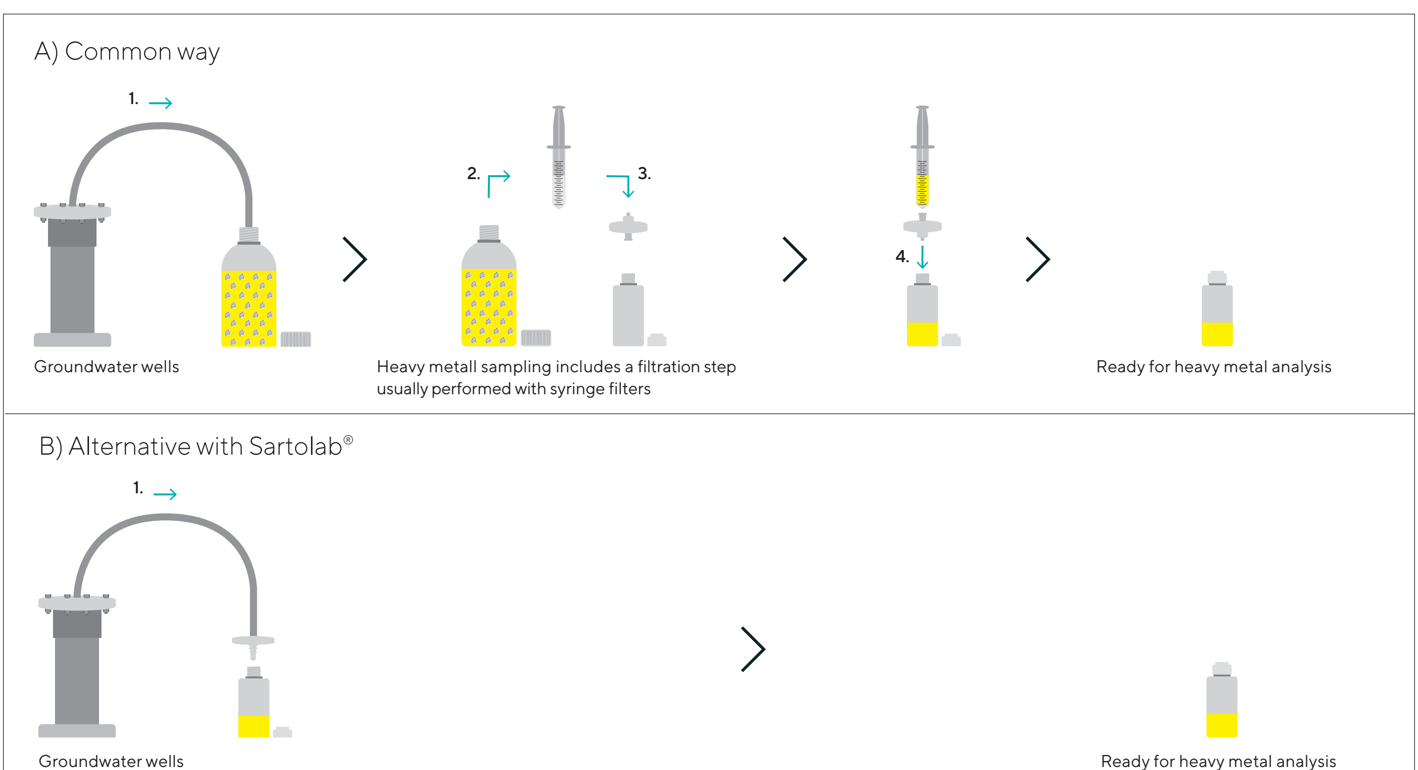

Fig. 1: Illustration of sampling and field filtration of groundwater using two different methods: A) by filtration using syringe filters B) by filtration using Sartolab® P20 Plus (in-line filter).

Diverse types of filters can be used for filtering groundwater samples, which need to be selected according to the specific sample volume and the suspended particulate load of the sample. The present study tests Sartolab® P20 Plus in-line filters that are designed for water samples in the liter range and with a high particulate load.

Within the scope of this study, the filtration efficiency of Sartolab® P20 Plus in turbidity measurements before and after filtration and the filter's throughput was investigated and compared with that of standard syringe filters. Additionally, the study investigated the potential release of heavy metals from the filter material, as well as the recovery of the analytes after filtration.

Materials and Methods

The filtration capacity of Sartolab® P20 Plus was characterized by measurement of throughput and reduction of turbidity. Furthermore, the potential adsorption of elementals by the filter material after contact with the drinking water sample spiked with an elemental standard was studied. Finally, an elemental extractables profile was obtained.

The following filters were used for the study; refer to Table 1.

Table 1: Filters tested in the study categorized by materials used for final filters and pre-filters and their effective filtration area (EFA).

	Sartolab® P20 Plus Order No. 18076-N	Syringe Filter Type A	Syringe Filter Type B
Pre-filter	quartz*	No	No
Final filter	0.45 µm PES	0.45 µm CA	0.45 µm CA
EFA	20 cm^2	4.91 cm^2	6.2 cm^2

* Also available without a pre-filter, but not considered in this study.

Fig. 3: Defined clay-suspension: 2.02 g clay/2 L, homogenized using a disperser, with a turbidity of 910 NTU on average.

Throughput and Turbidity

A clay suspension with a mass concentration of 1 g/L was prepared to determine the throughput. For this purpose, 2.02 g of clay was weighed and dispersed in 2 liters of reverse osmosis (RO) water using an Ultra-Turrax homogenizer. The clay suspension (Figure 3) was then filtered at a constant force of 34 N (Newton) through the respective test filter. The throughput was determined three times. The filtrate volumes were measured during the filtration run at distinct time points: 0 s, 10 s, 20 s, 40 s, 70 s, 130 s, 190 s, 310 s, 430 s and 550 s. At the time points of 430 s and 550 s, no values were determined for the syringe filters type A and B due to filter blockage.

The turbidity of the initial clay suspension was measured by a turbidimeter; that of the respective final filtrates, in a quadruple determination.

Adsorption and Release of Heavy Metals

The release of potential heavy metal extractables was studied using ICP-MS, and the mercury analytic was performed with CV-AAS. For that purpose, samples of 100 mL of Arium® Mini ASTM type 1 water after filtration were prepared, acidified, and measured with the respective analytical method. The results of the filtered RO water were compared to the results of RO water that did not come in contact with the filter material.

The potential adsorption of heavy metals after filter contact was investigated by ICP-OES, and analysis of mercury was carried out using CV-AAS. For this purpose, drinking water samples were spiked with a defined concentration of a heavy metal analytical standard. A portion of 100 mL of the spiked samples was filtered, acidified, and analyzed. These results were compared with the analytical results of samples that had not been in contact with the filter material. Additionally, Sartolab® P20 Plus filters without the pre-filter were used for comparison in order to investigate the influence of potential adsorption on the pre-filter composed of quartz. The recovery rate was determined, and the respective measurement uncertainty was applied.

All filters were flushed with 100 mL of Arium® Mini ASTM type 1 water before the samples were prepared.

Results and Discussion

Throughput

When the total throughput of each filter type was compared, Sartolab® P20 Plus clearly achieved higher values than those of both syringe filter types (Figure 4). While both syringe filter types showed similar throughputs of approximately 3 mL/cm², Sartolab® P20 Plus exhibited a throughput of approximately 5 mL/cm², meaning that nearly double the volume was filtered by its constant filtration area (EFA).

Therefore, groundwater can be readily sampled in at least 100 mL volumes all in one filtration step using a single Sartolab® P 20 Plus device to prepare filtrates for heavy metal analytics.

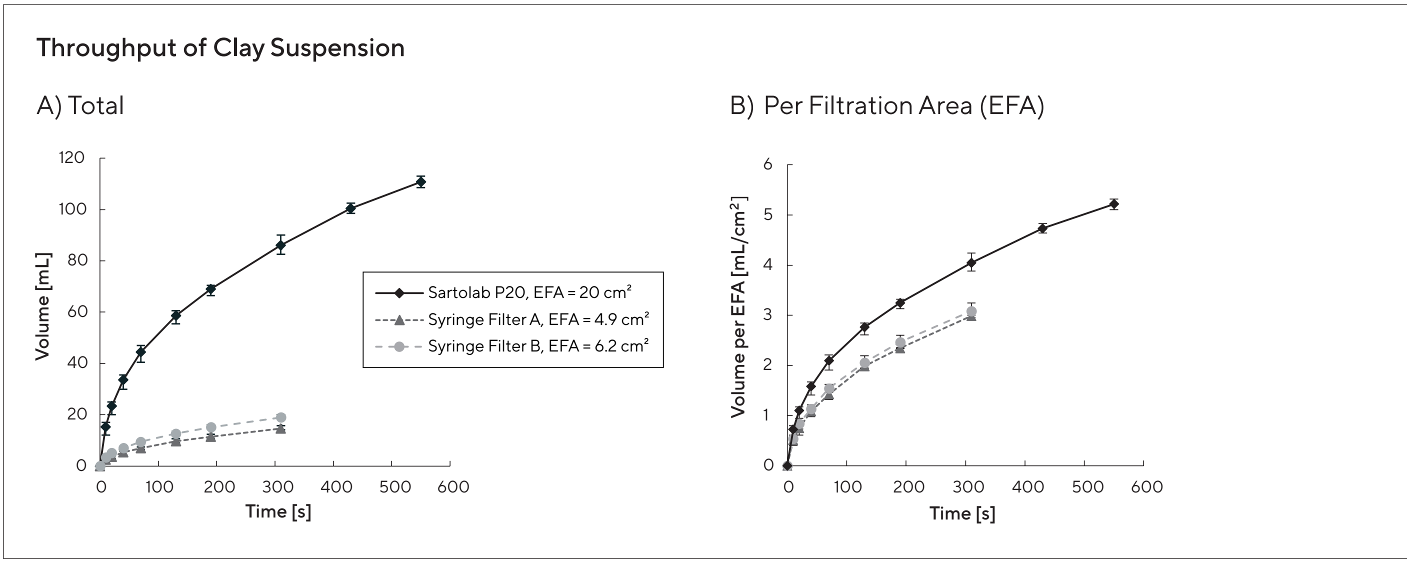

Fig. 4: The throughput of three different filter types was determined by filtering a worst-case clay suspension (2.02 g clay/L). Each throughput was evaluated per total device (A) and per effective filtration area (B). In both categories, Sartolab® P20 Plus showed the highest throughput values.

Turbidity

The clay suspension used as a defined source for the filtration experiments showed a turbidity of 910 NTU (Figure 5A). During filtration of the clay suspension, all filter types tested clearly reduced the turbidity by more than two powers of ten. Nevertheless, significant differences among the three filter types could be observed (Figure 5B). While syringe filters A and B showed a turbidity of 5.07 NTU and 3.77 NTU after filtration of 15 mL and 19 mL, respectively, the Sartolab® P20 Plus filter unit showed the lowest turbidity with 1.24 NTU after filtration of 110 mL. The differences observed might be explained by a different structure of the 0.45 µm CA membranes compared to PES membranes and by the utilization of a pre-filter composed of quartz fibers. This higher filtration capacity by utilization of a pre-filter accelerates sampling of groundwater that contains a higher content of humic substances.

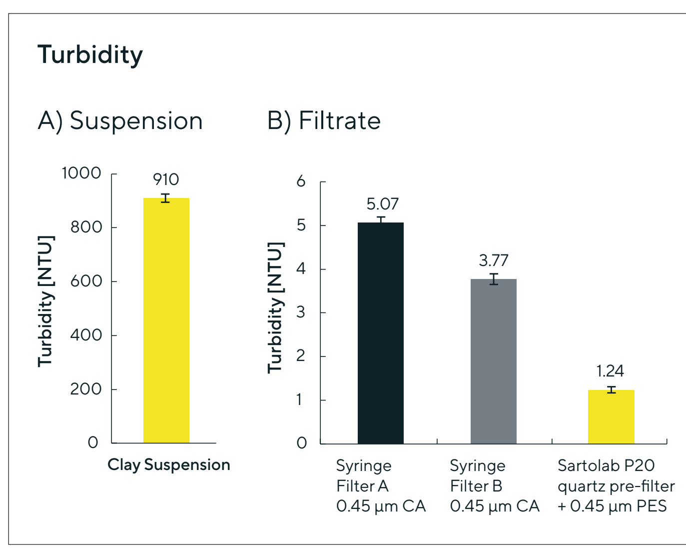

Fig. 5: The turbidity was determined for the initial clay suspension (A) and for the filtrates of three different filter types (B). While all three filter types reduced the turbidity by more than two powers of ten, Sartolab® P20 Plus showed the lowest turbidity.

Extractables Profile of Sartolab® P20 Plus

To evaluate the release of elemental extractables from the Sartolab® P20 Plus filtration device into purified water (RO water), the concentration of 30 different metal ions were analyzed by ICP-MS screening and CV-AAS. Samples after filter contact (Sartolab® P20 Plus) were compared with the unfiltered sample blanks (Table 2). While most of the elements were below the limit of quantification (LOQ), five elements – Ca, Cu, K, Na, and Zn – were determined to be slightly above the LOQ.

From a regulatory point of view, the values determined here are lower than the limits. Sartolab® P20 Plus shows high purity regarding the release of metal ions. This outcome is explained by the pureness of plastic and quartz microfiber materials used for production of Sartolab® P20 Plus and by a rinsing step of 100 mL of ultrapure water before sampling. Under actual field conditions prior to sampling, intensified rinsing with water from the same source is performed.

Table 2: The release of 30 metal ions from Sartolab® P20 Plus was determined by filtering 100 mL of ultrapure Arium® water ASTM type 1. Extractables results show that Sartolab® P20 Plus is suitable for the filtration of groundwater with regard to the respective guidelines: European Council Directive 98/83/EC[4] on water for human consumption, German Groundwater Ordinance (GrwV) and the limits of the United States Environmental Protection Agency (EPA).

Elements	LOQ [µg/L]	Blank [µg/L]	Sartolab® P20 Plus Extract [µg/L]	European Union 98/83/EC Limits [µg/L]	German GrwV Limits [µg/L]	United States EPA Limits [µg/L]
Aluminium	10	< 10	< 10	-	-	-
Antimony	1	< 1	< 1	5	-	6
Arsenic	1	< 1	< 1	10	10	10
Barium	0.5	< 0.5	< 0.5	-	-	2000
Beryllium	1	< 1	< 1	-	-	4
Lead	1	< 1	< 1	10	10	15
Boron	5	< 5	< 5	1	-	-
Cadmium	0.2	< 0.2	< 0.2	5	0.5	5
Calcium	10	< 10	60	-	-	-
Chromium	1	< 1	< 1	50	-	100
Iron	3	< 3	< 3	-	-	-
Potassium	50	< 50	160	-	-	-
Cobalt	0.2	< 0.2	< 0.2	-	-	-
Copper	1	< 1	1	2	-	1.3
Magnesium	10	< 10	< 10	-	-	-
Manganese	1	< 1	< 1	-	-	-
Molybdenum	1	< 1	< 1	-	-	-
Natrium	50	< 50	130	-	-	-
Nickel	1	< 1	< 1	20	-	-
Mercury	0.2	< 0.2	< 0.2	1	2	2
Selenium	1	< 1	< 1	10	-	50
Silver	5	< 5	< 5	-	-	-
Strontium	1	< 1	< 1	-	-	-
Tellurium	1	< 1	< 1	-	-	-
Thallium	0.2	< 0.2	< 0.2	-	-	2
Vanadium	2	< 2	< 2	-	-	-
Zinc	2	< 2	6	-	-	-
Tin	1	< 1	< 1	-	-	-

The extractables profile of Sartolab® P20 Plus does not contain any critical heavy metal concentrations according to the respective guidelines: European Council Directive 98/83/EC[4] on water for human consumption, the German Groundwater Ordinance (GrwV) and the limits of the United States Environmental Protection Agency (EPA).

Recovery

Sartolab® P20 Plus filter were examined for recovery of 19 metal ions, which were spiked in three distinct levels in a drinking water sample (Figure 6). The uncertainty of measurement was utilized to evaluate whether recovery would be most probable in the range of 100%. Overall, the results indicated that there is no measurable effect on the concentration of metal ions by using a Sartolab® P20 Plus filtration device. This outcome applies to all spike concentrations of 10, 50, and 200 µg/mL with one exception. Considering measurement uncertainty, zinc shows a slightly reduced recovery with 81.2% at a spike level of 10 µg/mL. Although the analyte zinc is not relevant for groundwater analysis according to GrwV, this can be explained either by an individual measurement deviation or by adsorption of zinc to the filtration unit at a low spike level.

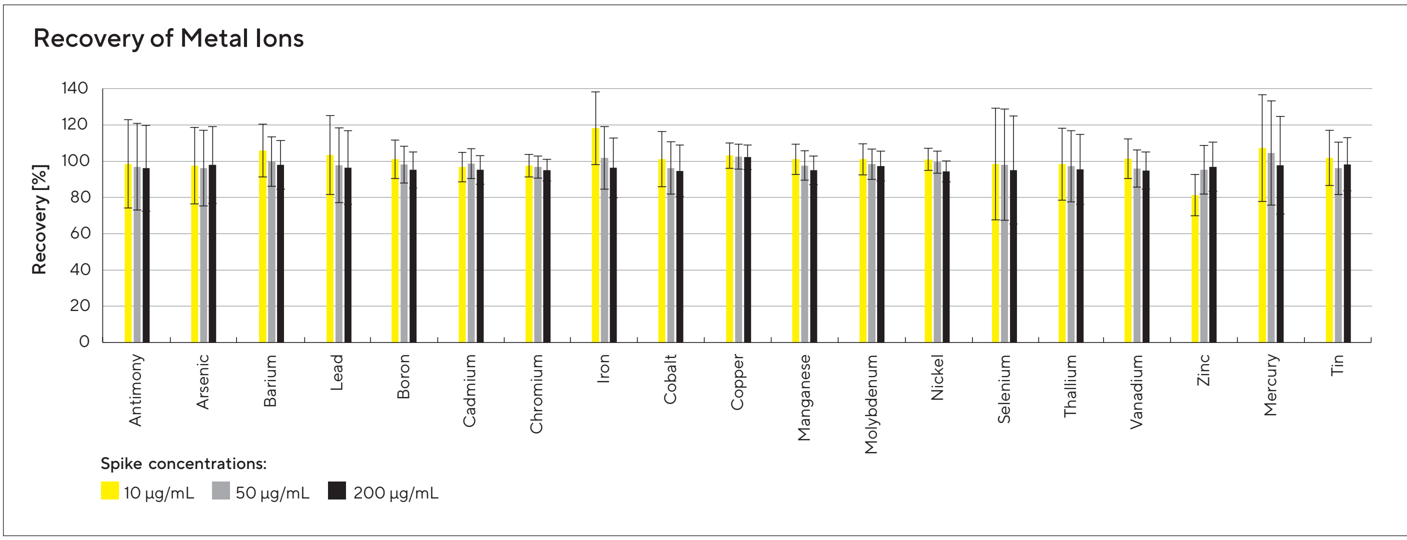

Fig. 6: Recovery of metal ions at three different metal ion spike concentrations (10, 50, and 200 µg/mL) was determined after filtration of a 100 mL sample. Drinking water was used as the sample matrix. Error bars show the uncertainty of measurement (n=1).

Conclusion

In this study, we examined Sartolab® P20 Plus filters for their suitability in filtering groundwater samples based on sample throughput, reduction of turbidity, release of extractables and recovery of metal ion analytes. The throughput and reduction of turbidity for Sartolab® P20 Plus are clearly superior to those for syringe filters due to the higher filtration area of Sartolab® P20 Plus and its additional quartz-fiber pre-filter. The more than 10-fold throughput enables in-line sampling directly from the groundwater source to the sample container without an intermediate step and supports the statements from users that Sartolab® P20 Plus extraordinary simplified groundwater sampling. Furthermore, Sartolab® P20 Plus did not release or retain any relevant amounts of dissolved metal ions so that these filter units do not affect the analysis of groundwater.

Acknowledgements

Special thanks go to Dr. Katharina Strelau and Andreas Brosig from Eurofins Umwelt Ost GmbH Jena for conducting throughput and turbidity experiments and for providing organizational support, and to Dr. Heike Böhme and Axel Ulbricht from Eurofins Ost GmbH Freiberg for sample analysis according to DIN EN ISO 17294-2 and DIN EN ISO 12846, as well as to Stephanie Schweizer of Sartorius for her constructive support.

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[2] Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration
[3] German Groundwater Ordinance
[4] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption

Abbreviations

98/83/EC	Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption
CA	Cellulose acetate
CV-AAS	Cold vapor atom absorption spectroscopy
EFA	Effective filtration area
EPA	United States Environmental Protection Agency
GrwV	Grundwasserverordnung (German Groundwater Ordinance)
ICP-MS	Inductively coupled plasma – mass spectrometry
ICP-OES	Inductively coupled plasma – optical emission spectrometry
LOQ	Limit of quantification
NTU	Nephelometric turbidity unit
PES	Polyethersulfone
RO	Reverse osmosis

Germany
Sartorius Lab Instruments GmbH & Co. KG
Otto-Brenner-Straße 20
37079 Göttingen
Phone +49 551 308 0

USA
Sartorius Corporation
565 Johnson Avenue
Bohemia, NY 11716
Phone +1 631 254 4249
Toll-free +1 800 635 2906

For further information, visit
www.sartorius.com

Status: 12 | 2020