

Cation Conductivity: Facts and Fiction

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ABSTRACT

Cation exchangers are of paramount importance to reliable conductivity readings. They come in all shapes and sizes and each and every type has its advocates. The purpose of the paper is to separate facts from fiction and shed light on such issues as rinse down, temperature effects and response time.

INTRODUCTION

The conductivity of makeup, feedwater and condensate after passage through a column of strongly acid cation exchanger resin is the most important single chemical measurement parameter used in steam generating power plants. There are many reasons for the preference for this method. The corresponding ASTM standard [1] mentions: "The equipment for this test method can be considered more rugged and adaptable to installation under plant operating conditions than the more accurate laboratory methods such as ion chromatography and atomic absorption."

Due to the large variety of different equipment and supplies on the market, such as columns of many shapes and volumes, resins, conductivity sensors and instruments, it may be difficult for the user of such equipment to judge the importance or unimportance of simple operational parameters such as flow rate, response speed, good installation practice and more. These concerns are addressed in [1]. Several instrument manufacturers also provide information and explanations. A few of these issues will be discussed in this paper.

SHAPE AND SIZE OF THE CATION EXCHANGER COLUMN

In the newsletter of one instrument manufacturer, these recommendations and information are given: "When monitoring cation conductivity, the optimum diameter for a resin column is 1 $\frac{5}{8}$ in (41.3 mm). This assures maximum effectiveness of the resin at a flow rate of 100 mL · min⁻¹ to 200 mL · min⁻¹. By contrast, a 2 $\frac{1}{2}$ in to 3 $\frac{1}{2}$ in (63.5 mm to 88.9 mm) column is less efficient and has a much greater

hold-up volume. Detectable changes in the sample chemistry, therefore, take longer to materialize at the analyzer cell" [2].

And in [3]:

1. At lower design than (flow) design velocities, resin performance is less effective, and the cations will not be totally removed.
2. The hold-up volume of the column causes a severe time lag before a representative sample reaches the analyzer. The result is that when an upset occurs, it can be 15 to 60 minutes before the upset is detected.

How can we judge these recommendations and translate them into information of real specific value? In [1] a column of 1 $\frac{5}{8}$ in (41.3 mm), length 12 in (304 mm) is proposed. The recommended flow rate is 100 mL · min⁻¹ to 200 mL · min⁻¹. In an effort to improve the handling when exchanging exhausted columns, the concept of resin bottles was introduced a few years ago (see [Figure 1](#)).

The use of a bottle as a resin container for cation conductivity measurement is certainly an improvement in regard to easy operation, because it hardly takes more than a few seconds, even for unskilled personnel, to exchange a bottle with spent resin for a new one.



Figure 1: Catcon bottle used as an ion exchange column with a flow cell for two conductivity sensors with integrated needle valve and digital flow meter.

However, a question remains: Can a column which deviates significantly in size and form from the ASTM version (see [Table 1](#)) produce meaningful and comparable results?

Type of Column	Diameter [mm]	Length [mm]	Volume [mL]	Flow Rate [mL · min ⁻¹]
ASTM	42.3	305	408	100–200
Catcon Bottle	89	160	1 000	100–200

Table 1: Comparison of size of ASTM and Catcon bottle columns.

FLOW RATE AS AN IMPORTANT OPERATIONAL PARAMETER

One of the key factors in the operation of any ion exchanger is the flow rate for a specific ion exchange column volume. This translates to linear speed of the water in that particular column.

In a product specification sheet [4] one resin manufacturer recommends a linear speed of 40 m · h⁻¹, but for condensate purification, up to 120 m · h⁻¹ are permitted for that particular cation exchange resin with a bed height of 80 cm.

Another manufacturer recommends between 100 m · h⁻¹ and 150 m · h⁻¹ for a bed height of 100 cm [5].

The resin manufacturers define an upper limit on the linear speed of the water but leave out a lower limit. Why?

The major influence of a high linear water speed is to decrease the time available for the ion exchange reactions to occur as the water passes through a column. Even more specific: The key factor for a complete ion exchange is a sufficient residence time of every small and finite volume of the sample within the active layer of an ion exchange column ([Figure 2](#)).

For an 80 cm layer of the S100 G1 resin at a permitted maximum linear flow speed of 120 m · h⁻¹ the residence time is $3\,600 \cdot 0.8 / 120 \text{ m} \cdot \text{h}^{-1} = 24 \text{ s}$. This applies to a new resin column; if we look at an almost exhausted column where three quarters of the bed height is spent, the residence time in the remaining active layer drops to only 6 seconds! If the residence time becomes too short, the ion exchange process will be incomplete, which renders the ion exchange column unusable unless regenerated or refilled with new resin.

The required residence time to meet the resin manufacturer's specifications can also be calculated for a given flow rate and column volume if the water volume between the bulk of the resin beads is known ("hold-up volume"). This can be easily done by weighing exactly one liter of

resin filled up with water and then subtracting the weight of the same drained sample ([Table 2](#)).

The two resins show almost the same hold-up volume of approximately 300 mL per 1 000 mL resin.

[Table 3](#) shows the calculated sample residence times for two different cation column volumes. For an ASTM-type

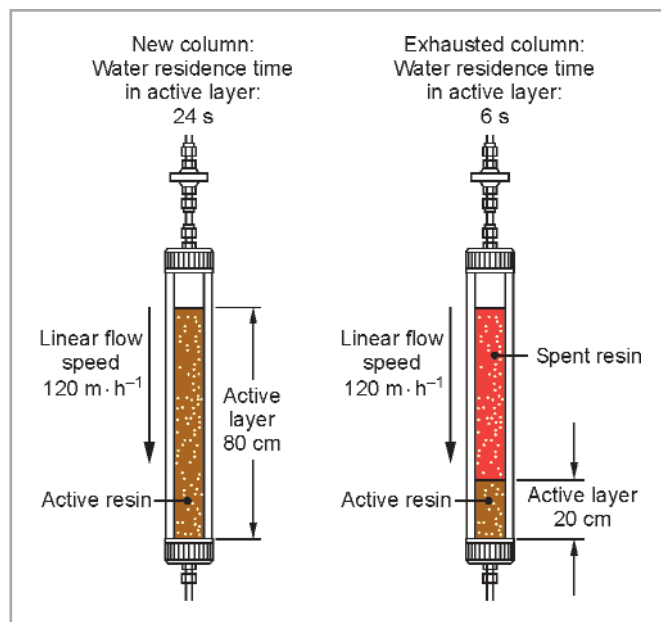


Figure 2: Change of sample residence time within an active resin layer at constant linear flow speed: new vs. exhausted column.

Strong Acid Cation Exchanger with Indicator Dye	Empty Space between the Beads [mL per L resin]
Lanxness® (Bayer) Lewatit® S100 G1	294
SWAN cation exchange resin	287

Table 2: Volume of space between the exchanger beads ("hold-up volume" of a resin volume of 1 L) for two different types of cation exchange resins used in cation conductivity measurements.

Resin Volume of Columns with Lewatit S100 G1	Calculated Residence Time of a Sample [min:s]
ASTM Type 408 mL	1:12
Catcon Bottle 1 000 mL	2:56

Table 3: The sample residence times for a flow rate of 100 mL · min⁻¹ in a 1 000 mL Catcon bottle with S100 G1 resin and an ASTM-type column with a resin volume of 408 mL. Hold-up volume / sample flow rate = residence time

column with a resin volume of 408 mL the residence time is approximately 2.5 times shorter than in the 1 000 mL column. Both times apply to unused columns and are higher than required by the manufacturers' specifications!

Response Speed

The calculated residence time applies of course also to the time required for a contamination to travel through the column, consequently the sample residence time equals more or less the response time lag to get a first output signal change after the sample impurity has entered the column.

A short response time lag is a very desirable feature, but on the other hand the resin capacity is also consumed at a rate 2.5 times faster in the ASTM column.

A practical test of the response time lag of the 1 000 mL bottle is shown in *Figure 3*. There is a good correlation between the predicted and the measured results.

Obviously the two most important parameters for response speed in cation conductivity equipment are resin volume, or more correctly the associated hold-up volume, and the sample flow rate. It is of secondary importance whether the column is long in size with a small diameter or short with a larger diameter as long as the volume remains the same.

Let's go back to the aforementioned sentence: "The result is that when an upset occurs, it can be 15 to 60 minutes before the upset is detected" [5]. This should be commented upon as follows: a response time lag of 60 minutes at a flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$ implies a column volume of more than 20 L, which is unrealistic. It is much more likely that these huge delays are a consequence of an insuffi-

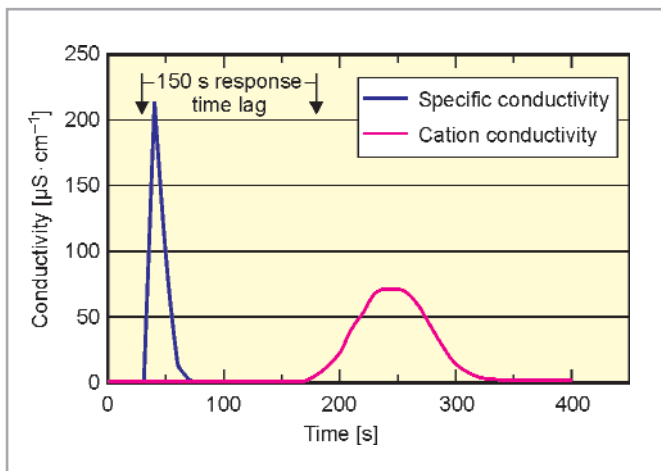


Figure 3: Response time lag of a Catcon bottle, 1 000 mL strongly acidic cation exchange resin SWAN, sample flow rate $100 \text{ mL} \cdot \text{min}^{-1}$, injection of 4 mL 0.01 M KCl solution into sample line, response time lag approx. 150 s.

cient sample flow. This highlights again the importance of a constant on-line monitoring of a correct sample flow rate [6–9].

Ionic Leaching

All ion exchange resins contain ionic impurities after the manufacturing process, unless these have been washed out more or less in separate procedures. In cation conductivity measurements this may be a very annoying phenomenon because the ionic impurities will add to an otherwise correct measurement and make it read too high. This is an issue in all cases where the spent resin is disposed of and replaced by a new supply. It may be necessary to increase the flow rate considerably above the ASTM recommended level of $100 \text{ mL} \cdot \text{min}^{-1}$ to $200 \text{ mL} \cdot \text{min}^{-1}$ for the first few days in order to dilute the leached out compounds enough to get reasonable cation conductivity readings. Different resin batches of the same resin type can show quite different behavior when put into operation. In some batches of the rinse down, this behavior can be visible for several days [10].

A practical evaluation can be seen in *Figure 4*. This is a comparison of the rinse down time of three different cation exchange resins.

The upper curve shows the rinse down properties of a new, off-the-shelf resin (S100 G1). The middle curve is also a new resin, which has been rinsed after the manufacturing process (SWAN). The lowest curve is a used, carefully regenerated and rinsed sample of the same type and batch as that of the upper curve (S100 G1).

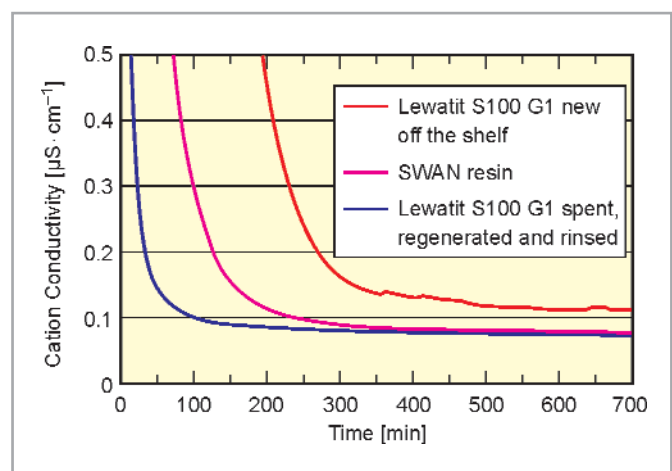


Figure 4: Rinse down times of three different samples of strongly acidic cation exchange resin.
 instrument FAM Deltacon
 flow rate $6 \text{ L} \cdot \text{h}^{-1}$ ($100 \text{ mL} \cdot \text{min}^{-1}$)
 resin volume 1 000 mL
 sample demineralized water conductivity range $0.057 - 0.059 \text{ µS} \cdot \text{cm}^{-1}$

The somewhat longer first rinse down time of the new, off-the-shelf resin (upper curve, S100 G1) can be easily accepted, but the long-lasting elevated horizontal part may be problematic for achieving accurate cation conductivity measurements. Used and carefully regenerated and rinsed resins can deliver very good rinse down times. Where regeneration of spent resins is not possible, the use of rinsed and pre-packed material is a viable alternative.

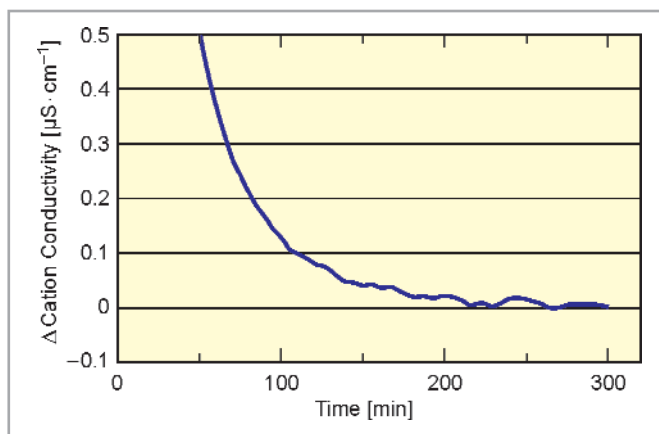
What kind of performance can be expected in real application in a power plant?

A typical graph is shown in *Figure 5*. A three-year-old resin sample stored in an original Catcon 1 000 mL bottle has been used in order to cover the worst case. The results are summarized in *Table 4*.

The ionic leaching can also be observed after the initial rinse down period, although much less prominent. It is mostly visible when the flow rate is changed. Such a test with different flow rates can be seen in *Figure 6*.

The ionic leaching versus sample flow rate is also shown in a graph in annex A2.1 of the ASTM standard [1]. According to the presented graph, a flow rate change from 100 mL · min⁻¹ (6 L · h⁻¹) to 200 mL · min⁻¹ (12 L · h⁻¹) will decrease the observed conductivity by an amount of 0.015 μS · cm⁻¹. These results have been obtained with pure water with a 0.055 μS · cm⁻¹ conductivity.

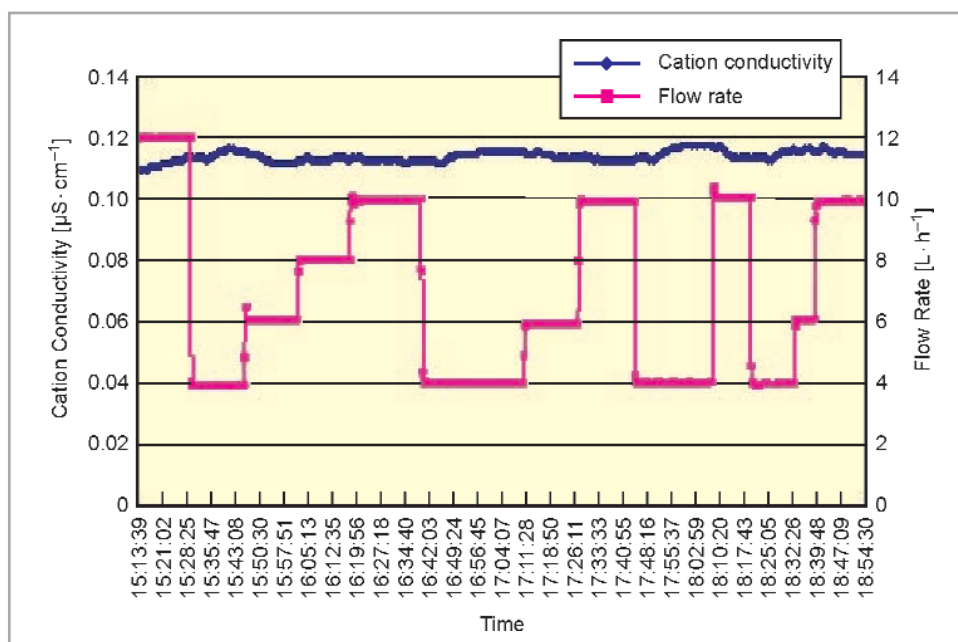
After an initial rinse down, in our graph (*Figure 5*) only small changes in the cation conductivity are visible, in spite of the large variation in the flow range between 4 L · h⁻¹ (66 mL · min⁻¹) and 12 L · h⁻¹ (200 mL · min⁻¹) with the Deltacon equipment. The changes are < 0.003 μS · cm⁻¹ and occur mostly at the very low flow rate of 66 mL · min⁻¹. They are smaller by a factor of 5 than the ASTM values with pure water.



*Figure 5: Rinse down time of an unused strongly acidic cation exchange resin (SWAN) stored for three years: conductivity difference to continuously running power plant monitor. Average sample conductivity 0.150 μS · cm⁻¹.
sample feedwater
flow rate 12 L · h⁻¹
resin volume 1 000 mL*

Cation Conductivity: Difference in Comparison with Final Value (power plant monitor) [μS · cm ⁻¹]	Rinse Down Time [min]
0.5	50
0.3	67
0.2	82
0.1	107

*Table 4: Rinse down time of an unused resin (SWAN). See the caption of Figure 5.
flow rate 12 L · h⁻¹
resin volume 1 000 mL*



*Figure 6: Cation conductivity as a function of the flow rate.
sample feedwater
flow rate test with varying flow rate after 12 h operation with a flow rate of 8 L · h⁻¹*

Fast Start up in Cycling Power Plants and the Cation Conductivity Equipment

The fast start up in cycling power plants represents a challenge to all equipment, including the analytical on-line instruments. In order to economize on expensive energy resources it is desirable to start the steam turbines as early as possible after steam is available, but not before the impurities in the early steam have decreased to an acceptable level in order to avoid corrosion problems in the turbine.

Because the cation conductivity is an important if not the most important parameter for the start up decision, the question arises: Does the steam quality lag behind or is it just the cation conductivity instrument?

To answer this question the flow through a cation conductivity instrument with a rinsed down resin supply was stopped. One downtime was 15 hours and a second one lasted for 17 days. The flow was then started again and the rinse down times recorded and compared to the stable results of the well-equilibrated power plant monitor running on the same sample stream (final value); *Figure 7*. The results are summarized in *Table 5*.

Conclusion: After an initial rinse down period of new resin the cation conductivity monitor is ready to deliver meaningful results within a few minutes after a shut down period of a few hours up to several weeks.

Temperature Problems in Cation Conductivity Equipment

The ASTM publication proposes constant temperature equipment for adjusting the influent sample temperature to $25\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$. According to ASTM there are two reasons to do this:

1. The cation resin loses its ability to maintain its holding power with increases in temperature.
2. Early conductivity equipment without microprocessors does not have the possibility to compensate the large temperature effects of pure water.

Comment on the first point: This effect is hardly noticeable in the temperature range between $20\text{ }^{\circ}\text{C}$ and $35\text{ }^{\circ}\text{C}$ in cation conductivity measurements.

Comment on the second point: This has completely changed with modern instrumentation and the use of correct temperature compensation algorithms; see *Figure 8*.

In practical applications neither of these two effects are really visible as can be readily observed in *Figure 6*.

The Influence of Sampling Systems

The remark in the VGB PowerTech Guidelines: "Poor sampling gives poor results" [9] can be directly applied to the measurement of cation conductivity.

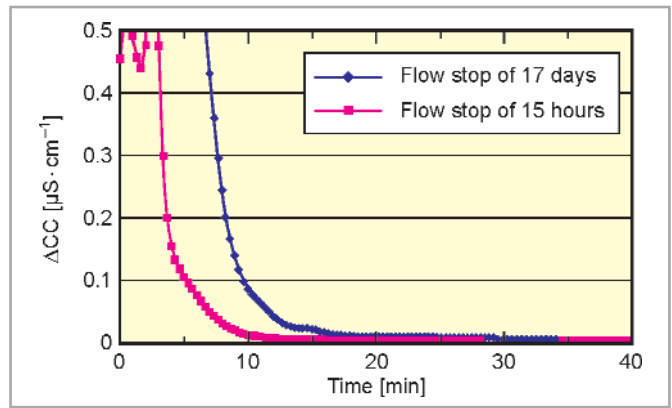


Figure 7: Cation conductivity during rinse down after flow stop for 15 hours and 17 days. Average sample conductivity $0.121\text{ }\mu\text{S}\cdot\text{cm}^{-1}$.

ΔCC measured cation conductivity – final value
 instruments FAM Deltacon and a continuous power plant instrument
 sample feedwater
 resin volume 1 000 mL

ΔCC [$\mu\text{S}\cdot\text{cm}^{-1}$]	Rinse Down Time after a Flow Stop	
	for 15 h [min:s]	for 17 days [min:s]
0.5	3:00	7:00
0.3	3:20	7:40
0.2	3:40	8:40
0.1	5:20	9:40

Table 5: Difference between the measured and the final feedwater cation conductivity (ΔCC).

instrument FAM Deltacon
 resin volume 1 000 mL
 sample feedwater, average cation conductivity $0.121\text{ }\mu\text{S}\cdot\text{cm}^{-1}$

Note: This phenomenon is not covered in [1].

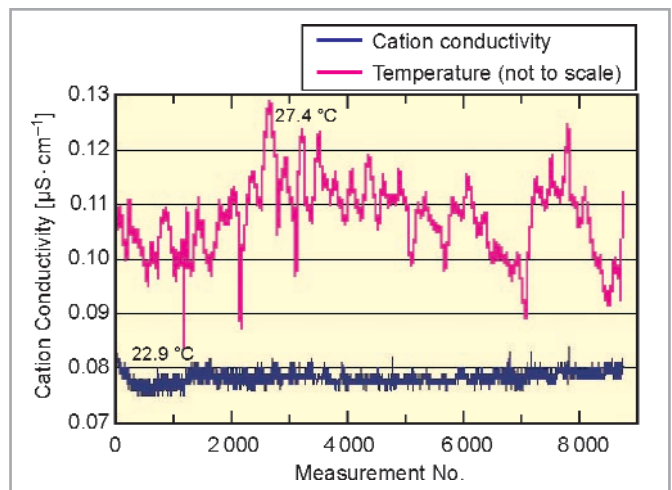


Figure 8: Condensate cation conductivity and sample temperature fluctuations (31-day period).

Basic problems in sampling systems are

- leaks (especially connectors and valves)
- very long sample lines
- inappropriate tubing material.

We would like to focus on unsuitable tubing material or more precisely on the use of plastic tubing in cation conductivity measurements. In contrast to metal tubing all plastic tubing is to a certain extent permeable to gases. Pieces of plastic tubing are frequently used to connect cation exchange columns to sample lines and conductivity sensor flow cells. Most quick connectors can only be used with flexible plastic tubing. This kind of connection is permeable to carbon dioxide and will lead to a false increase in the real conductivity. *Figures 9 and 10* show existing examples of connections made with flexible tubing.

A practical evaluation of the permeation rate for flow rates from $25 \text{ mL} \cdot \text{min}^{-1}$ to $125 \text{ mL} \cdot \text{min}^{-1}$ of different plastic tubing materials is given in [11]. The author demonstrates the increasing diffusion rate by CO_2 and oxygen as follows:



Figure 9: Cation exchange column connected by silicone rubber tubing.



Figure 10: Lower end of column with leaky silicone tubing.

PVDF (polyvinylidene difluoride) < Nylon (a polyamide) < polypropylene < FEP (perfluoro-ethylene-propylene) ~ polyethylene ~ PFA (perfluoroalkoxy polymer).

Conclusion in [11]: "For the absolute least contamination by gas permeation, 316SS should be used. The best plastic tubing for limiting both oxygen and CO_2 permeation is PVDF, with Nylon a close second for high purity water applications...."

We made a simple test with a few samples of different plastic tubing in a system with demineralized water (see *Figure 11*). The more flexible the tubing, the higher the permeability to carbon dioxide, the worst being silicone rubber. In addition, the flexible PVC (polyvinyl chloride) tubing contains ionic impurities which only rinse down after many hours of operation. If necessary, short pieces of FEP and Nylon tubing can be used as a sample connection to cation conductivity instruments.

CONCLUSION

The measurement of cation conductivity includes a set of technical parameters with a strong mutual influence. A few of the important ones have been briefly discussed. However, other important aspects remain, including initial cost of equipment and even more the cost of ownership. Quality, reliability, and simplicity of handling and maintenance must be carefully balanced with the available personnel resources.

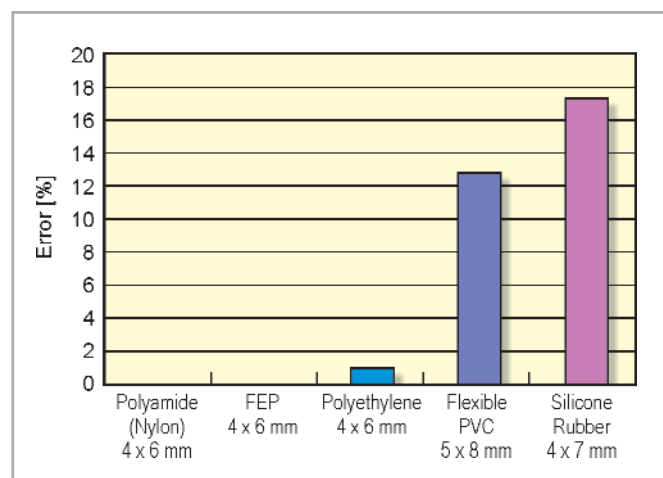


Figure 11: Increase in specific conductivity (n %) caused by diffusion of ambient carbon dioxide through different types of tubing into a sample stream.

flow rate $100 \text{ mL} \cdot \text{h}^{-1}$
 tubing length 65 cm
 basic conductivity $0.100 \mu\text{S} \cdot \text{cm}^{-1}$

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