

Stable Low Level Conductivity Standards

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Abstract

Many scientists are concerned about the virtual non-existence of low-level conductivity standards. Where such standards have been reported, independent studies have shown them to be unstable, non-matrix compatible or not reaching the low conductivity levels required for modern measurement. This paper presents stability data on an aqueous 5µS/cm conductivity standard, which has never previously been reported, and introduces a stable, aqueous 1.3µS/cm conductivity standard that is new to science. Such standards address the concerns previously raised and provide analysts with improved confidence in their low-level analytical measurements.

1 Introduction

The measurement of low-level conductivity is carried out in a wide range of industries, e.g. power generation, pharmaceutical and semiconductor manufacture and is principally performed on aqueous samples. In such instances, critical decisions are made based upon these conductivity readings and so it is essential that analysts can not only achieve the correct conductivity test results, but also prove the validity of their results.

For Quality Control and validation purposes then good quality, low-level conductivity standards are required. The criteria for the selection of such standards being:

- Accurately determined conductivity value
- Traceable to primary standards
- Matrix-matched to the sample (these are almost exclusively aqueous)
- Proven stability
- Readily available

In order to overcome the instability of low-level aqueous conductivity standards, caused by absorption of atmospheric carbon dioxide, a number of manufacturers offer conductivity standards containing organic solvents, e.g. propanol or glycerol^(1,2). These standards require a high degree of temperature control during use, due to their very high temperature coefficients of variation^(2,3) and will also introduce matrix errors. It would be preferable to be able to use low-level, aqueous conductivity standards; however, a number of recent publications^(4,5) have concluded that low-level conductivity standards with proven stability are not commercially available.

Gingerella and Jacanin⁽⁴⁾ conducted stability studies on a number of manufacturers' low-level conductivity standards and found that their performance did not match the manufacturers' stability claims. These authors called for manufacturers of low-level conductivity standards to prove that the performance of their products complied with their published specifications and expiry dates and to revise their specifications (if necessary) or to remove their products from the market.

Reagecon have conducted a detailed stability study of their complete range of aqueous conductivity standards (from 1.3 to 500,000µS/cm). These standards are manufactured using an innovative process that is designed to counteract the effect of absorption of atmospheric carbon dioxide on the conductivity value of the standards. This paper details the findings of this study for the low-level standards - 1.3 & 5µS/cm. The results of this study address the concerns raised by Gingerella and Jacanin and show that Reagecon's conductivity standards comply with the selection criteria required for low-level conductivity standards. The study investigated the effect of the following factors on the stability of Reagecon's conductivity standards:

- Head-space in the bottle
- Storage temperature
- Bottle material

Reagecon's published specifications and expiry dates for their low-level conductivity standards are shown in Table 1.

Conductivity Standard value ($\mu\text{S}/\text{cm}$ at 25 °C)	Expiry Date (From Q.C. approval)	Specified Tolerance ($\mu\text{S}/\text{cm}$ at 25 °C)
5.00	6 months	4.95 – 5.05 ($\pm 1\%$)
1.30	3 months	1.25 – 1.35

Table 1: Published Specifications and Expiry Dates of Reagecon’s Conductivity Standards

2 Experimental

2.1 Apparatus

The apparatus used for this study consisted of a water bath, a precision conductance analyser, a conductivity cell and a certified thermometer. The conductivity cell used was a Jones-type cell consisting of parallel, platinized-platinum plates mounted at opposite sides of a glass sample chamber. The temperature of solutions during measurement was controlled at 25.00°C \pm 0.05°C. The apparatus, the voltage and the frequency of the A.C. potential applied across the conductivity cell were selected to minimise measurement uncertainty. The calculated expanded uncertainty associated with the test results is < 0.30% (coverage factor, $k = 2$).

2.2 Procedure

2.2.1 Cell Constant Determination

The cell constant was determined as per the procedures outlined in ASTM D1125⁽⁶⁾. The materials used to prepare the calibration solution were potassium chloride (NIST SRM999a) and deionised water (conductivity 1.081 $\mu\text{S}/\text{cm}$). The cell constant was determined to be 0.1054 cm^{-1} . The calculated expanded uncertainty associated with the assignment of the cell constant is < 0.18% (coverage factor, $k = 2$).

2.3 5 $\mu\text{S}/\text{cm}$ Test Samples

Reagecon’s 5 $\mu\text{S}/\text{cm}$ conductivity standard is packaged in 500mls bottles. It is intended that the user can extract multiple aliquots for use over the period from opening the bottle up to the expiry date stated on the bottle label. The effects of bottle headspace, storage temperature and bottle material for the 5 $\mu\text{S}/\text{cm}$ standard were investigated.

2.3.1 Effect of Bottle Head-Space

Parallel testing was conducted on the same batch of conductivity standard packed in “fresh bottles” and “working bottles”. The fresh bottles were filled, sealed and capped as per

Reagecon’s Standard Operating Procedures. The working bottles were filled to 80% capacity and capped but not sealed. These working bottles were packaged to represent the expected conditions experienced by conductivity standards throughout their working life.

For each fresh bottle test, a new bottle was removed from storage and the bottle was disposed of after testing. When testing working bottles, a test aliquot was removed and then the bottle was re-capped and put back into storage. Both types of bottles were stored at room temperature, away from direct light.

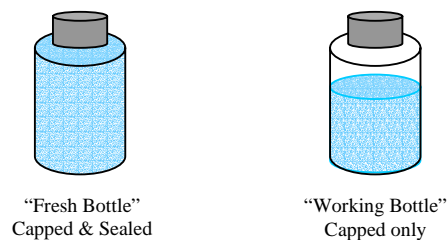


Figure 1: Packaging of Test Samples

2.3.2 Effect of Storage Temperature

To investigate the effect of storage conditions, working bottles stored at 4°C were included in the parallel testing. The samples were packaged and tested as described in 2.3.1.

2.3.3 Effect of Bottle Material

Gingerella and Jacanin’s⁽⁴⁾ study showed that the difference between measured and stated conductivity was greatest for manufacturers that packaged their conductivity standards in glass bottles. For this reason, glass bottles were not investigated in this study. Parallel tests were performed on the HDPE bottles currently used for Reagecon’s conductivity standards and on PET bottles. Samples from the same batch of conductivity standard were packaged, stored and tested using the procedure for working bottles described in 2.3.1. The packaging and storage conditions of the 5 $\mu\text{S}/\text{cm}$ test samples are summarised in Table 2.

Bottle	Type	Bottle Material	Initial Fill Capacity	Storage Temperature
Bottle A	Fresh Full Bottle	HDPE	100 %	Ambient
Bottle B	Working Bottle	HDPE	80%	Ambient
Bottle C	Working Bottle	HDPE	80%	4°C
Bottle D	Working Bottle	PET	80%	Ambient

Table 2: Storage Conditions of Samples

2.4 1.3µS/cm Test Samples

Reagecon's 1.3µS/cm conductivity standard is packaged in single-use bottles - therefore stability tests were limited to tests on a series of freshly opened bottles of the same batch. These bottles were filled and capped in accordance with Reagecon's Standard Operating Procedures and were stored at room temperature, away from direct light. For each test, a fresh sample bottle was removed from storage and the bottle was disposed after testing.

2.5 Test Schedule

The conductivity of the 5µS/cm test samples was measured over a one-year period. Test measurements were taken weekly for the first 4 weeks of the trial, fortnightly from week 4 to week 12 and then every 4 weeks for the remainder of the trial. The conductivity of the 1.3µS/cm test samples was measured over a 14 week period. Test measurements were taken weekly for the first 4 weeks of the trial and fortnightly for the remainder of the trial.

3 Test Results

The results of the stability trial for the 1.3 & 5µS/cm are given in Tables 3 & 4.

Time (Weeks)	Conductivity (µS/cm)			
	Bottle A	Bottle B	Bottle C	Bottle D
0	5.000	5.000	5.000	5.000
1	5.017	4.998	4.999	5.130
2	5.028	5.004	5.089	5.146
3	5.023	5.024	5.124	5.207
4	5.012	5.026	5.093	5.239
6	5.025	5.031	5.112	5.234
8	4.991	4.975	5.124	5.186
10	5.000	4.993	5.156	5.235
12	4.987	5.034	5.122	5.298
16	5.008	5.023	5.192	5.347
20	5.001	4.982	5.191	5.393
24	4.973	4.997	5.206	5.484
28	4.968	4.975	5.217	5.527
32	4.979	4.948	5.229	5.544
36	4.970	4.965	5.221	5.633
40	4.951	4.947	5.163	5.701
44	4.952	4.974	5.202	5.741
48	4.925	4.921	5.151	5.775
52	4.926	4.929	5.244	5.760

Table 3: Measured Conductivity - Nominal 5µS/cm Samples

Time (Weeks)	Conductivity (µS/cm)	Time (Weeks)	Conductivity (µS/cm)
0	1.300	6	1.310
1	1.315	8	1.329
2	1.321	10	1.321
3	1.309	12	1.338
4	1.306	14	1.340

Table 4: Measured Conductivity - Nominal 1.3µS/cm Sample

4 Discussion

The results of this stability study are discussed under the following topics:

- Simulated Working Conditions - 5 μ S/cm samples.
- Effect of Storage Temperature - 5 μ S/cm samples.
- Effect of Packaging Bottle Material - 5 μ S/cm samples.
- Stability of 1.3 μ S/cm samples.

4.1 Simulated Working Conditions - 5 μ S/cm samples

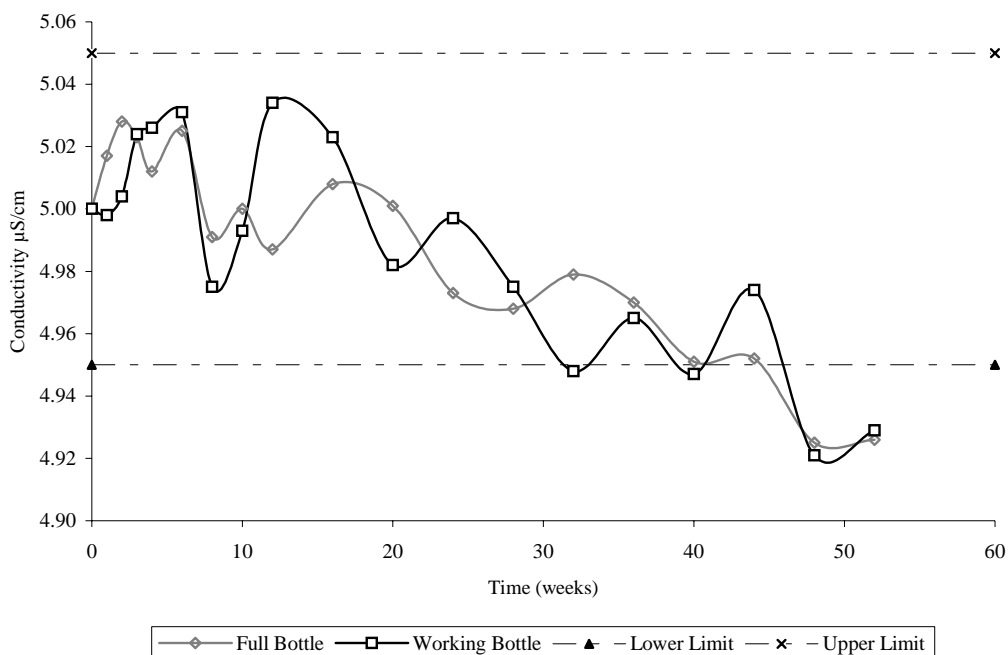
4.1.1 Discussion of Results

Throughout the working life of a typical bottle of conductivity standard, aliquots are periodically removed from the bottle and then the bottle is re-capped and placed back into storage. It is important for the analyst to have confidence in the manufacturer's stated value

for the standard until the solution is fully used or the stated expiry date is reached.

Graph 1 shows that for both working bottle samples and freshly opened bottle samples there is an initial rise in the measured conductivity value, followed by a steady drop in the measured conductivity value over the course of the stability study. The measured value of the working bottle samples falls outside the lower specification limit after 32 weeks, whilst the measured value of the fresh bottle samples falls outside the lower specification limit after 48 weeks.

Reagecon assigns an expiry date of 6 months from the date of Quality Control approval for batches of their 5 μ S/cm conductivity standards. This period is less than the interval elapsed before either the working bottle or fresh bottle samples give a measured value outside of Reagecon's published specification limits.



Graph 1: 5 μ S/cm Samples at Room Temperature

Conductivity of aqueous solution (μ S/cm at 25°C)	Concentration (μ g/L)		
	NaCl	HCl	NH ³
0.055	0	0	0
0.250	91	20.7	16.1
0.500	207	42.6	34.4
1.00	439	86	76
2.00	903	172	177
5.00	2295	430	638

Table 5: Effect of Trace Contaminants on the Conductivity of Ultra Pure Water⁽⁷⁾

4.1.2 Recommendations for the Storage and Handling of Conductivity Standards

Care must be exercised during the handling, storage and use of low-level conductivity standards to prevent exposure to trace contaminants. Such contaminants may be absorbed by the conductivity standard, leading to an increase in the ionic concentration and thus an increase in the conductivity value. Table 5 shows how the conductivity of ultrapure water is significantly increased by the introduction of various trace contaminants. Further guidance on handling of conductivity standards is given in the Reagecon publication "Practical Measures for Accurate Conductivity Measurement" by Barron and Ashton.

4.2 Effect of Storage Temperature

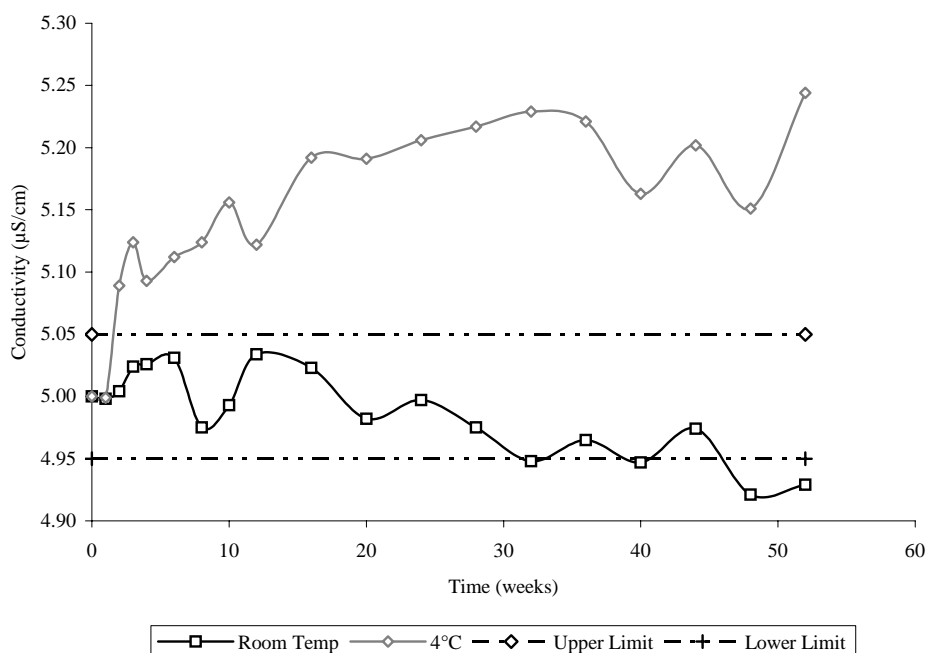
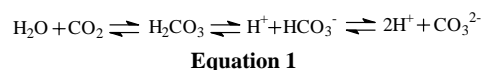
Graph 2 shows that the measured values of the samples stored at room temperature gradually fell over the period of the stability study, falling below the lower tolerance limit after 32 weeks. The measured values of the samples stored at 4°C show a rapid rise in the initial measured conductivity, followed by a steady increase in the measured conductivity over the course of the stability study. The measured

values of the samples stored at 4°C rise above the upper tolerance limit after 2 weeks.

Absorption of atmospheric carbon dioxide by a solution, as shown in Equation 1, will lead to an increase in ionic concentration and thus an increase in its conductivity.

The rise in the measured values of the samples stored at 4°C is due to absorption of carbon dioxide from the headspace of the bottle. Table 6 shows that the solubility of carbon dioxide in water is substantially higher at lower temperatures.

Due to the dependency of the value of conductivity standards on storage temperature, the authors recommend that conductivity standards are stored at room temperature, away from direct light. Storage at elevated temperatures is not recommended, as evaporation of the solvent may occur, leading to an increase in the solution's ionic concentration and thus an increase in the conductivity value.



Graph 2: Working Bottles Stored at Room Temperature and 4°C

Temperature (°C)	Weight of Carbon Dioxide (g) soluble in 100 g Water
0	0.3346
5	0.2774
10	0.2318
15	0.1970
20	0.1688
25	0.1449

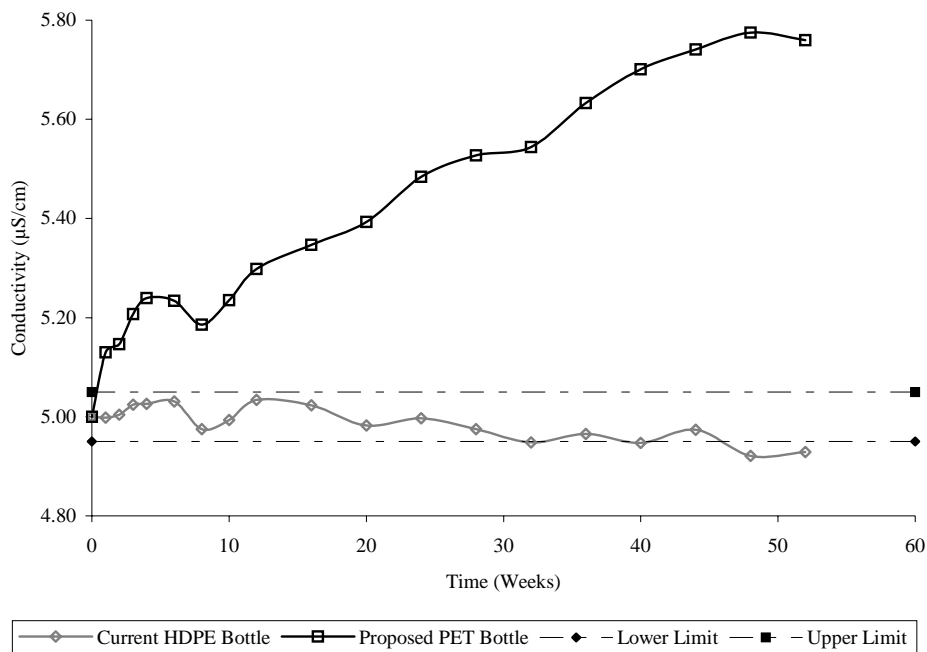
Table 6: Solubility of Carbon Dioxide in Water - Variation with Temperature ⁽⁸⁾

4.3 Effect of Packaging Bottles Material

Graph 3 shows that the selection of packaging bottle material is critical to the stability of low-level conductivity standards. The measured values for the test samples stored in PET bottles rose over the course of the study and all lie above the upper specification limit. The measured values for the test samples stored in HDPE bottles remain within the specification limit until week 32 of the study – at this point the measured value of the sample stored in PET is 5.544 $\mu\text{S}/\text{cm}$. The most likely cause of the measured rise in the conductivity

of the samples stored in PET bottles is absorption of plasticizers from the packaging bottle material.

Gingerella and Jacanin⁽⁴⁾ found that the measured conductivity of 10 $\mu\text{S}/\text{cm}$ samples supplied in glass bottles was significantly higher than that of 10 $\mu\text{S}/\text{cm}$ samples packaged in plastic bottles from the same manufacturer. This finding, combined with the findings of this study, demonstrates that manufacturers' selection of packaging material has a critical effect on the stability of low-level conductivity standards.

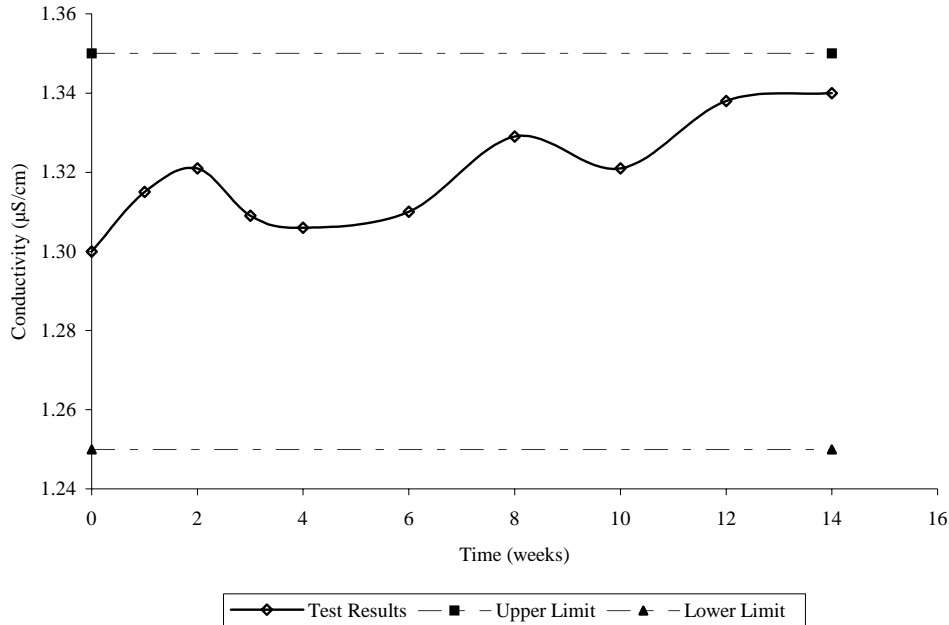


Graph 3: Working Bottles Packaged in HDPE & PET Bottles

4.4 Stability of 1.3 μ S/cm Samples

Reagecon's 1.3 μ S/cm conductivity standards are packaged in single-use bottles only. Consequently no investigation of working bottles was performed. Graph 4 demonstrates

that Reagecon's 1.3 μ S/cm standard remains within the published specification limits of $\pm 0.05\mu$ S/cm for the stated shelf life of 3 months.



Graph 4: 1.3 μ S/cm Samples Stored at Room Temperature

5 Conclusion

The results of the study described in this paper fully validate Reagecon's published shelf lives and specifications for their low-level conductivity standards.

The test results for the working, partially-full bottles of Reagecon's 5 μ S/cm conductivity standard demonstrate that analysts can have confidence in the integrity of this standard during its entire operational life. The test results for working bottles of Reagecon's 5 μ S/cm conductivity standard show a stability that exceeds the performance reported for freshly opened bottles of conductivity standards from alternative sources.

The test results for Reagecon's 1.3 μ S/cm conductivity standard validate the published specification and shelf life for this aqueous, low-level conductivity standard that is new to science.

Reagecon have answered the 'call to action' issued by Gingerella and Jacanin⁽⁴⁾, whose analysis showed that other manufacturer's low-level conductivity standards failed to match their published specifications and shelf lives. Reagecon's innovative manufacturing process and careful selection of packaging material means that Reagecon are the only manufacturer that is able to offer demonstrably stable, aqueous, low-level conductivity standards. The availability of these low-level conductivity standards means that, for the first time, analysts have access to the standards required for validating their low conductivity measurements and analysts can have significantly increased confidence in their low conductivity test measurements.

6 References

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- 4 M. Gingerella and J. A. Jacanin, "Is there an Accurate Low-Conductivity Standard Solution?", Cal Lab August 2000
- 5 Y.C.Wu and P.A. Berezansky, "Low Electrolytic Conductivity Standards", Journal of Research of the National Institute of Standards and Technology, 100, 521 (1995)
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- 8 J. A. Dean, "Lange's Handbook of Chemistry", 14th Edition, McGraw-Hill, Inc.

Biographical Notes:

John J Barron is Managing and Technical Director of Reagecon Diagnostics Limited. The company, which was founded in 1986, is the largest producer worldwide of Conductivity Standards and is also a major

producer of other chemical standards. Mr. Barron is an expert in several areas of analytical chemistry, including electro-chemical analysis, good laboratory practice (GLP) and chemical metrology. He has written and lectured extensively and is credited with several scientific discoveries including stable low-level conductivity standards.

Colin Ashton has worked in the Reagecon group since 1994 and is currently Head of the Chemical Metrology Department. A graduate of the University of Southampton, he has developed particular expertise in the development, stabilisation, manufacture and validation of cation, anion and electro-chemical standards. He has particular scientific interest in all aspects of on line chemical analysis and has lectured and published on several areas of this field.

This paper forms part of a comprehensive series of papers that the authors have written covering all of the practical requirements for accurate conductivity measurement. These papers and the authors' book, "A Practical Guide to Accurate Conductivity Measurement" are available at Reagecon's website - www.reagecon.com.

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