Evaluation of gasoline corrosivity

Wire Resistance Method

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Compatibility with Copper: ASTM D130

Designation: D130 – 19

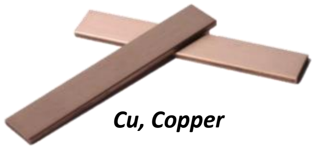
Federation of Societies for
Paint Technology Standard No. Dt-28-65
British Standard 4351

ASTM D130

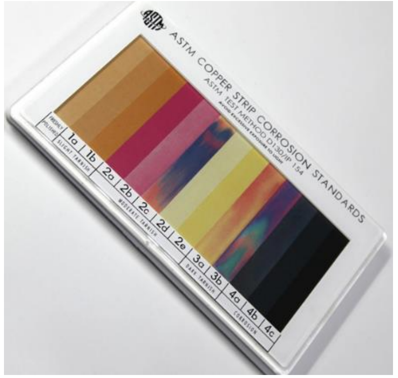
Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test[1]

This standard is issued under the fixed designation D130; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.



Cu, Copper



Report

- Test Duration (hrs.)
- Temperature (°C)
- Classification category (1,2,3 or 4)
- Classification description (a, b or c)

+ Easy to execute
+ Well accepted industry std
- Not Quantitative
- No kinetic information

Industry accepted modifications to ASTM D 130:

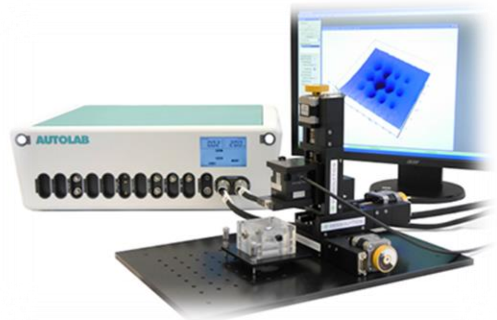
I. Measure of Cu released by means of ICP-AES (ASTM D5185) was introduce to provide quantitative information.

II. Extension of the test to 1000 hrs + Measure of Cu released over the time was introduce to provide kinetic information.

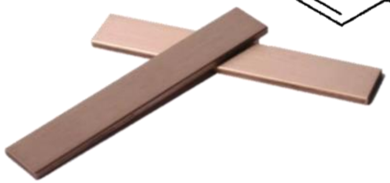
Limitations and misinterpretations of: ASTM D130[1]

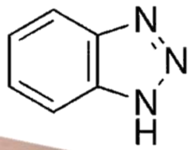
! In presence of surface-active molecules, as corrosion Inhibitors, ASTM D130 interpretation can be misleading

Benzotriazole base molecules are the most typical Corrosion inhibitor used in Lubricants industry to protect Cu and Cu alloys

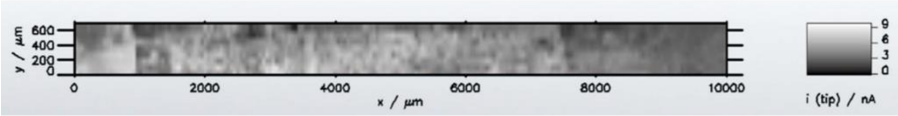


Scanning Electrochemical Microscopy





Adsorption of Benzotriazole on Cu



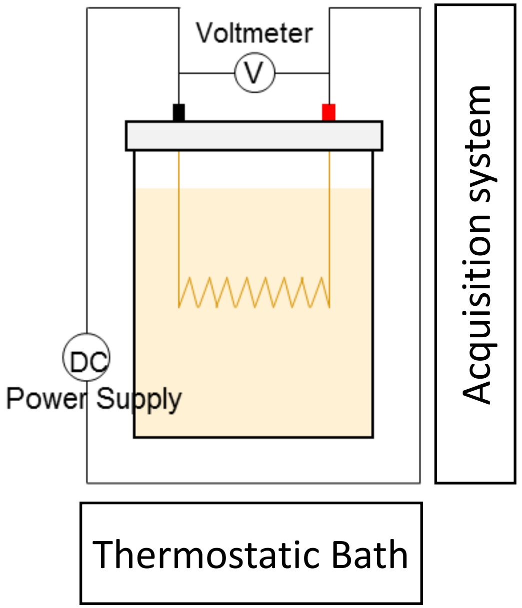
Tarnishing degree

[1]*Scanning electrochemical microscopy (SCEM) Principle and Application.*
Dr. Michaela Nabel. Metrohm Users Meeting 2019, Zofinghen.

Wire resistance method[2,3,4]: Principles

Despite the method is not yet an ASTM standard, **PLI** recognized its potentialities and **decided to invest resources to implement it** in house as **key method for e-fluids development** and technology selection.

Experimental Set-up



Outputs

$$Resistance = \frac{\rho Cu_T l}{\pi r^2}$$

$$r = \sqrt{\frac{\rho Cu_T l}{\pi \; Resistance}}$$

r *Copper wire radius (µm)*

ρCu_T *Resistivity of Copper at Testing Temp. T (Ωm)*

T *Temperature (°C) → Const. (Imposed/Measured)*

$\rho Cu_{20°C}$ *Resistivity of Copper at 20°C (Ωm) → Const.*

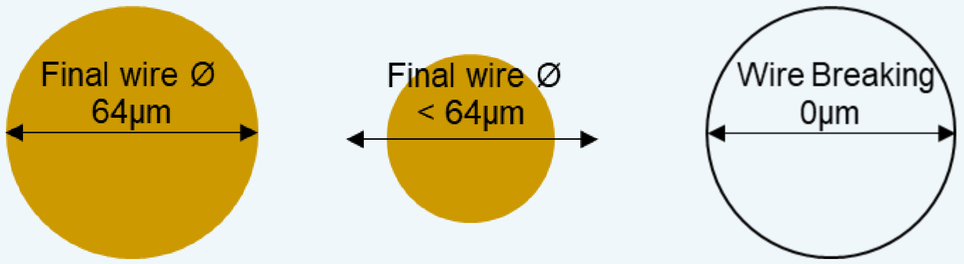
α *Coefficient of thermal expansion of Cu → Const.*

$$\rho Cu_T = \rho Cu_{20°C} + \alpha(T - 20)\rho Cu_{20°C}$$

l *Copper wire length (m) → Const.*

Practical meaning of the outputs

Ω Constant	***Ω Constant Increase***	***Ω Exponential Increase***
Ø Constant	***Ø Reduction***	***Wire braking***



Corrosivity: **No/Low**	Corrosivity: **Low/Medium**	Corrosivity: **High**
Cu compatibility: **++ High**	Cu compatibility: **+/- Medium/TBD**	Cu compatibility: **-- Poor**

[2] **New Insight on the Impact of Automatic Transmission Fluid (ATF) Additives on Corrosion of Copper**. *Michel P. Gahagan et al. International Journal of Automotive Engineering 7 (2016) 115-120*

[3] **Wire resistance method for measuring the carrion of copper by lubricating fluids**. *Gregory J. Hunt et al. Lubrication Science 29 (2017) 279-280*

[4] **Automatic transmission fluid corrosion inhibitor interaction with copper**. *Michel P. Gahagan et al. Lubrication Science 30 (2018) 301-315*

Materials & Methods

Fluids

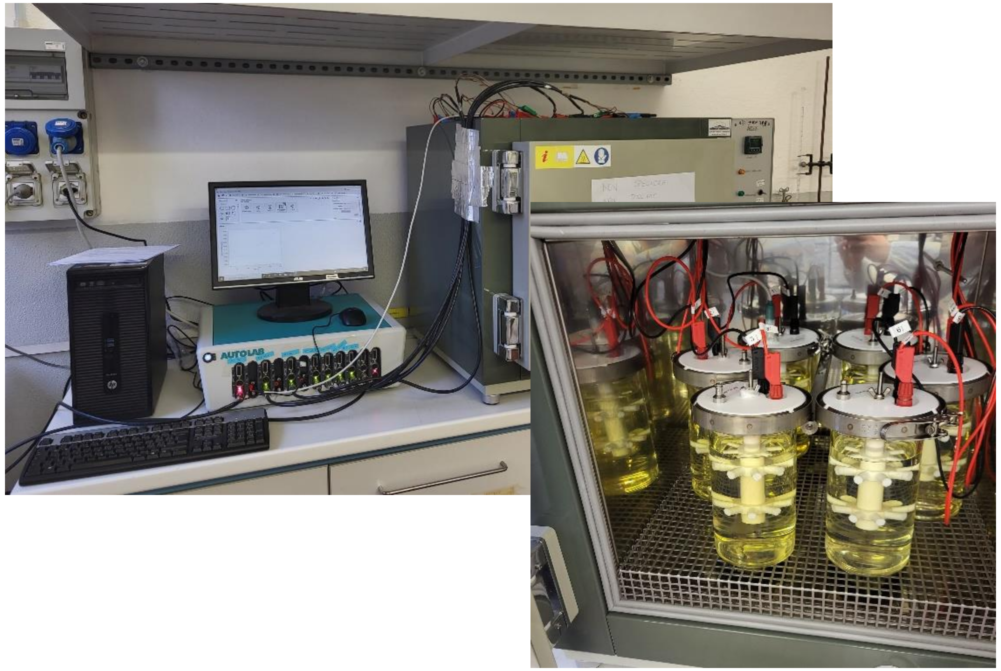
ID	Gasoline	Composition
S70	**E0**	Ethanol 0%
S55	**E10**	Ethanol 10%
S80	**E20**	Ethanol 20%
S36	**E100**	Ethanol 100%
S67	**A20**	Methanol 15% Ethanol 5%
S23	**M100**	Methanol 100%

ID	Gasoline	Composition
-	**E0 ref.**	Ethanol 0%
-	**E20 ref.**	Ethanol 10%

Wire materials

ID	Material	Composition	Radius r (µm)	Resistivity ρ 20°C Ωm	Coefficient of Thermal Expansion α (°C-1)
Cu	Copper	Cu 99.8+%	32	1.68E-08	3.68E-03
304SS	Stainless Steel AISI 304	Fe/Cr18/Ni10	37.5	7.20E-07	1.72E-05
430SS	Stainless Steel AISI 430	Fe81/Cr17/Mn/Si/C/S/P	25	6.00E-07	1.04E-05

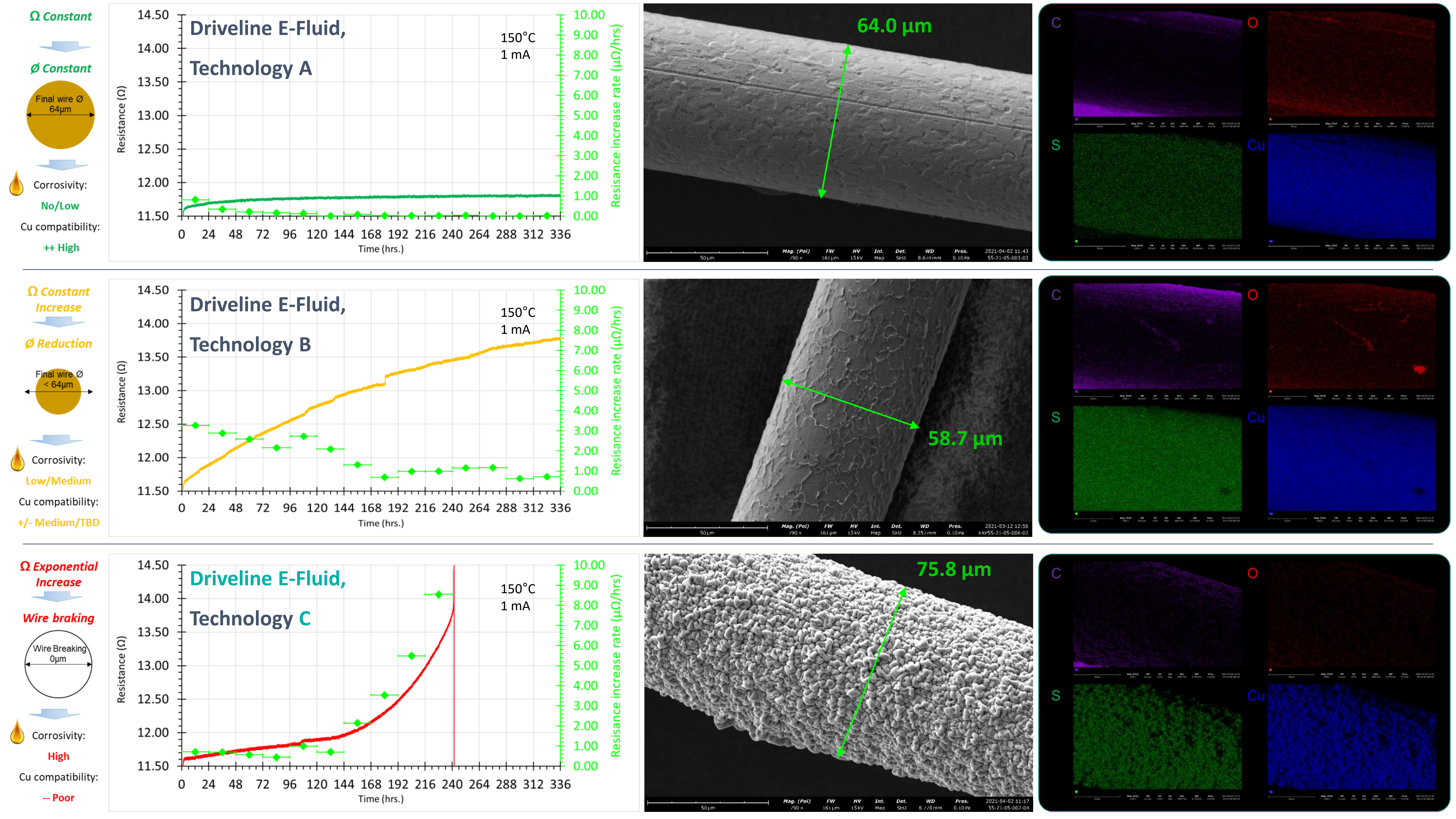
Experimental set-up



- **Metrohm Multi Autolab 101 +**
- **pX1000 Module** temperature meas.
- **Applied temperature:** 30°C.
- **Applied current:** 1 mA (constant).
- **Calibration:** 15 min w/o fluid
- **Sampling rate:** 20 s.
- **Test duration:** 336 hrs.
- **Fluid Volume:** 1100 ml.

Wire Resistance Method:

Typical results for driveline lubricants on copper

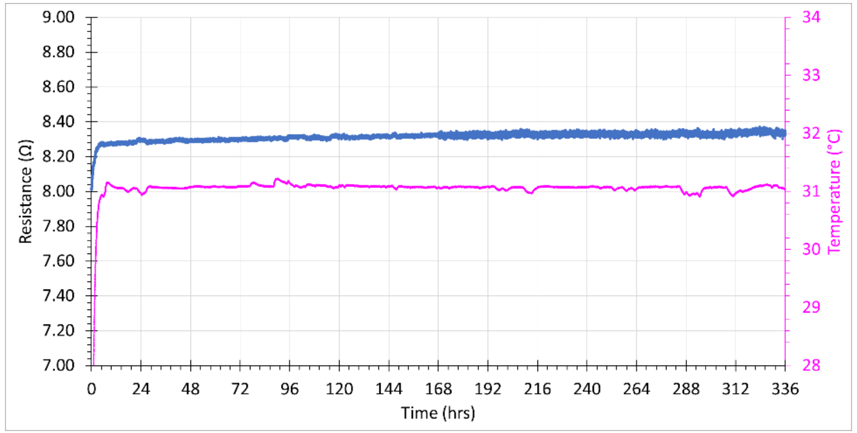

Ω Constant
Ø Constant
Final wire Ø 64µm
Corrosivity:
No/Low
Cu compatibility:
++ High
Driveline E-Fluid,
Technology A
150°C
1 mA
Resistance (Ω)
Resisance increase rate (µΩ/hrs)
Time (hrs.)
64.0 µm
C
O
S
Cu
Ω Constant Increase
Ø Reduction
Final wire Ø < 64µm
Corrosivity:
Low/Medium
Cu compatibility:
+/- Medium/TBD
Driveline E-Fluid,
Technology B
150°C
1 mA
Resistance (Ω)
Resisance increase rate (µΩ/hrs)
Time (hrs.)
58.7 µm
C
O
S
Cu
Ω Exponential Increase
Wire braking
Wire Breaking 0µm
Corrosivity:
High
Cu compatibility:
-- Poor
Driveline E-Fluid,
Technology C
150°C
1 mA
Resistance (Ω)
Resisance increase rate (µΩ/hrs)
Time (hrs.)
75.8 µm
C
O
S
Cu

Wire Resistance Method:

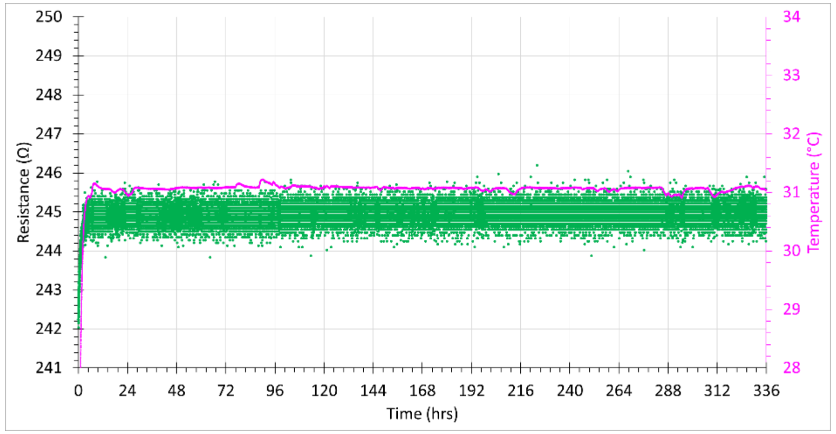
Results for gasoline on copper & stainless steel

Wire Resistance evolution in E0 ref. gasoline

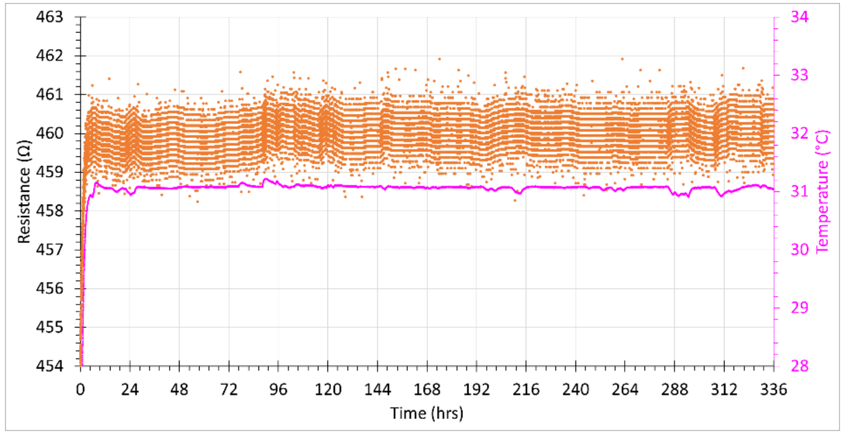
Copper (Cu)



Stainless steel 304 (SS304)



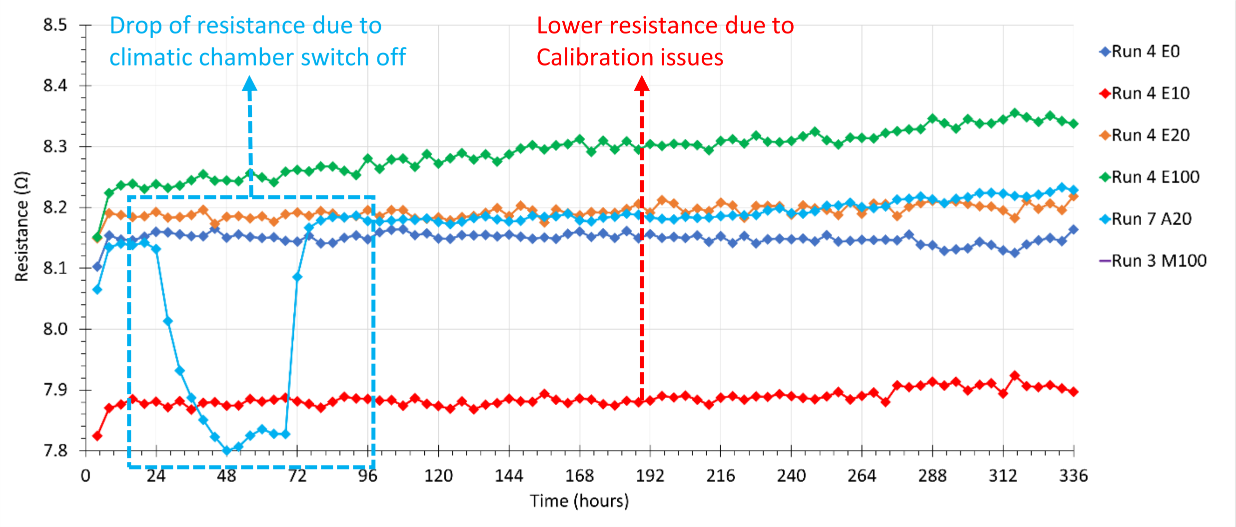
Stainless steel 430 (SS430)

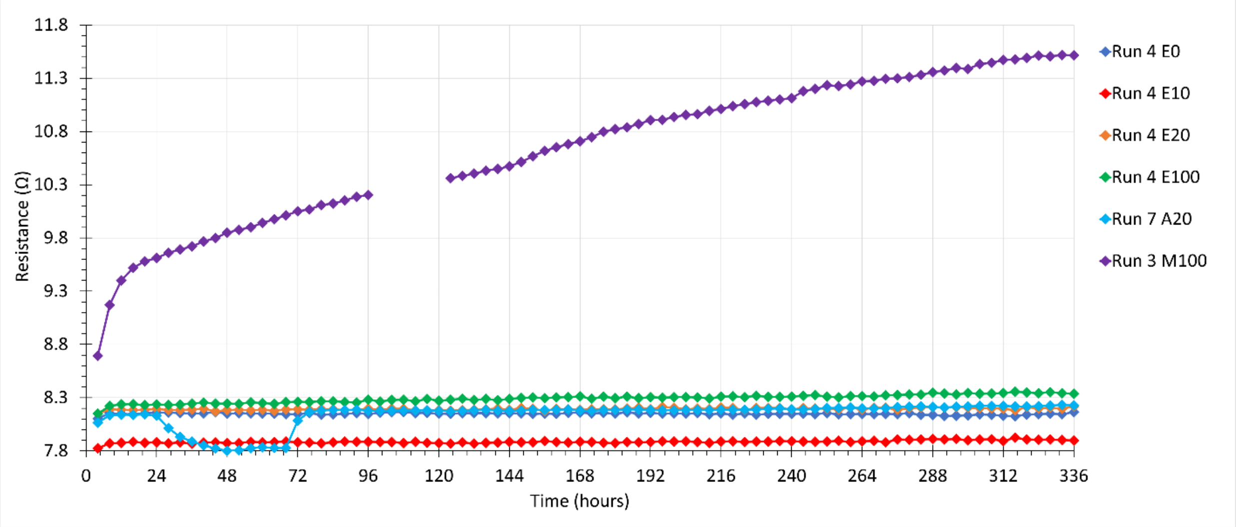


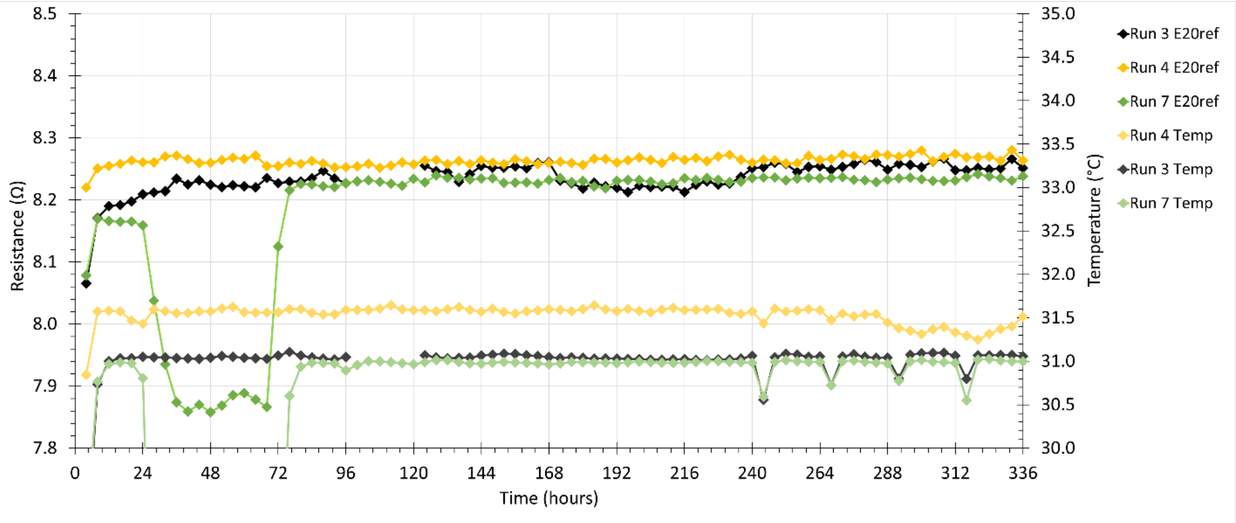
- Resistance evolution of Cu, SS304 and SS430 in contact with E0 gasoline has negligible growth over 1 week of exposure at 30°C.
- Cu signal is as low noise (≈ 0.1 Ω).
- SS304 & SS430 signals are very noisy ≈ 2 Ω & ≈ 4 Ω respectively.
- Based on the data reported trend, data treatment has been carried by averaging resistance values over 4 hours intervals..

Cu Wire Resistance evolution in gasoline

Except in M100 Cu resistance growth is very limited in all gasolines. Despite this, by analysing the slopes it is possible to extract the following trend of corrosivity: E0 < E20 / E10 < A20 < E100 << M100

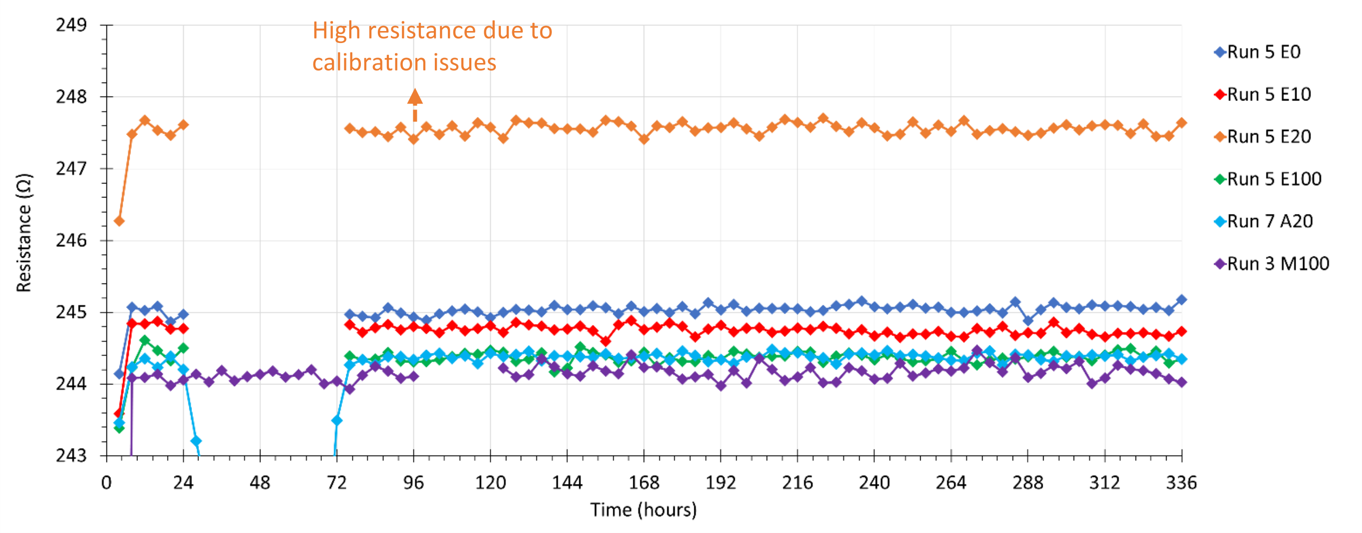


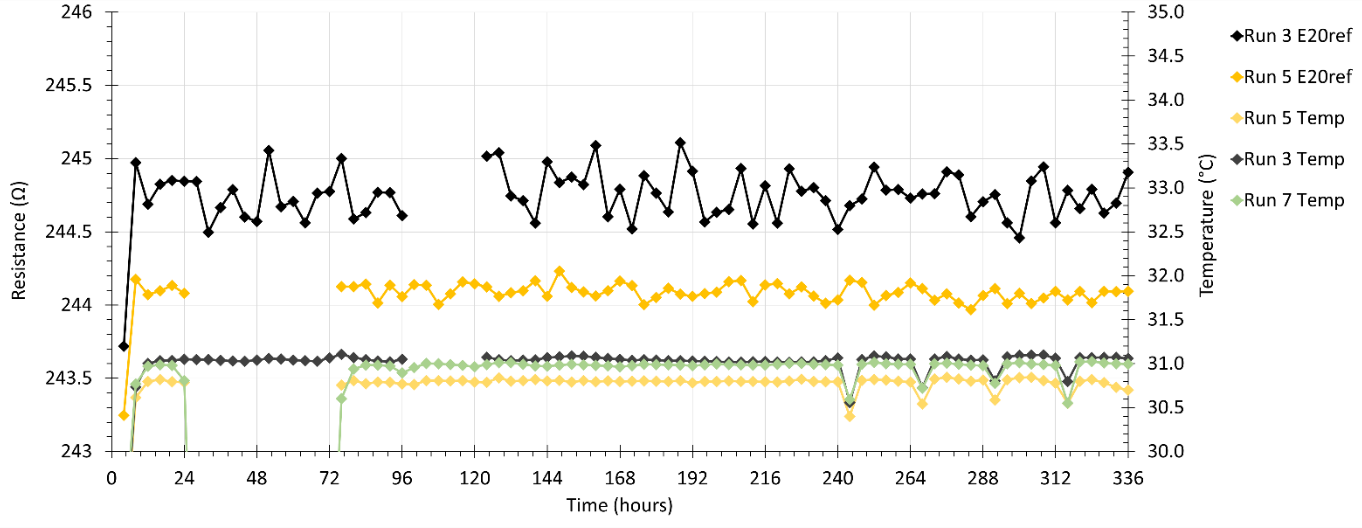




Run	ID	Gasoline	Composition	Resistance increase (Ω/hrs)
4	S70	E0	Ethanol 0%	-5.00 E^{-5} ≈ 0
4	S55	E10	Ethanol 10%	1.01E^{-4}
4	S80	E20	Ethanol 20%	7.01 E^{-5}
4	S36	E100	Ethanol 100%	3.38 E^{-4}
7	S67	A20	Methanol 15% Ethanol 5%	2.17 E^{-4}
3	S23	M100	Methanol 100%	6.18 E^{-3}
3	-	E20 ref	Ethanol 20%	9.86 E^{-5}
4	-	E20 ref	Ethanol 20%	3.25 E^{-5}
7	-	E20 ref	Ethanol 20%	2.43 E^{-5}

SS 304 Wire Resistance evolution in gasoline

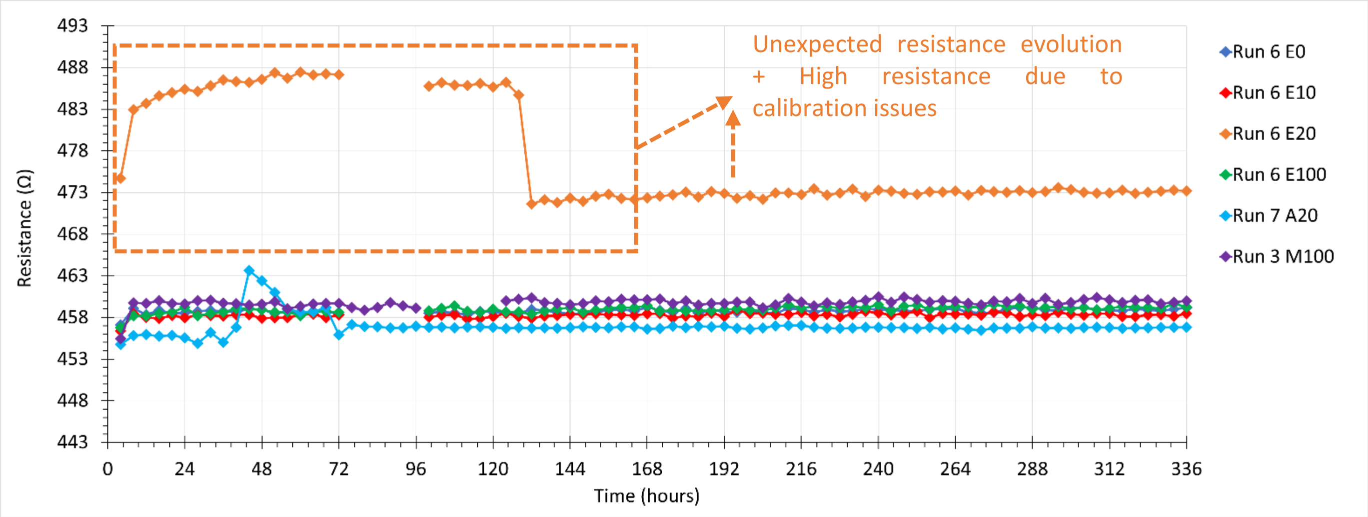


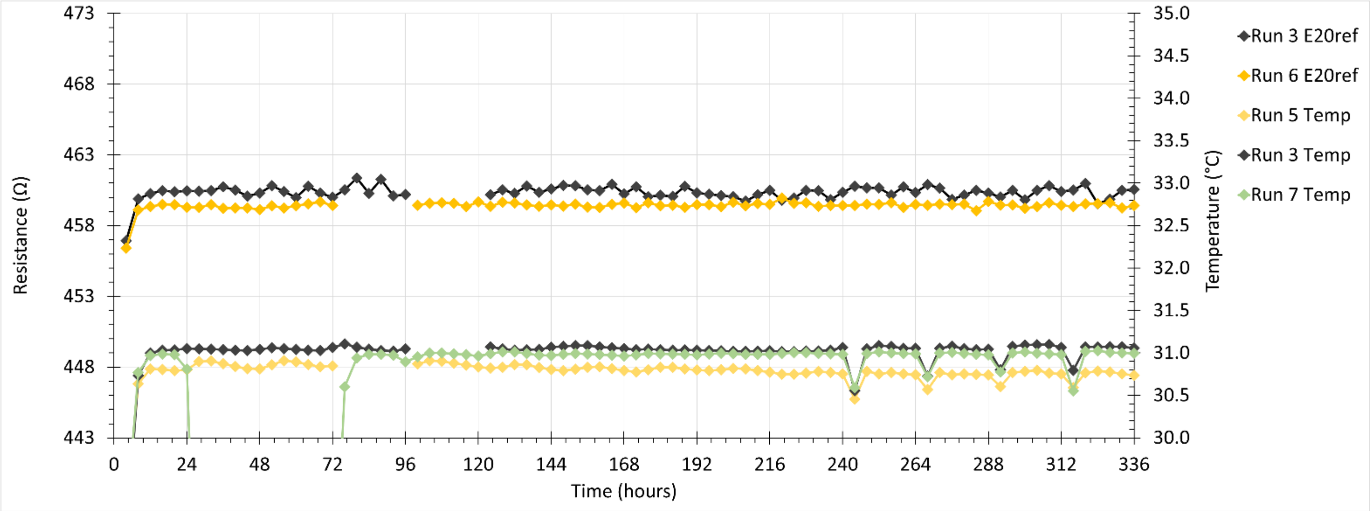


- SS304 resistance growth is negligible in all gasolines.
- The analysis of the slopes do not highlight any corrosivity trend.

Run	ID	Gasoline	Composition	Resistance increase (Ω/hrs)
5	S70	E0	Ethanol 0%	3.65 E^{-4}
5	S55	E10	Ethanol 10%	-3.62 E^{-4} ≈ 0
5	S80	E20	Ethanol 20%	3.24 E^{-5}
5	S36	E100	Ethanol 100%	9.36 E^{-5}
7	S67	A20	Methanol 15% Ethanol 5%	7.88 E^{-5}
3	S23	M100	Methanol 100%	1.28 E^{-4}
3	-	E20 ref	Ethanol 20%	-2.83 E^{-4} ≈ 0
5	-	E20 ref	Ethanol 20%	-2.19 E^{-4} ≈ 0
-	-	-	-	-

SS 430 Wire Resistance evolution in gasoline





- SS403 resistance growth is negligible in all gasolines.
- The analysis of the slopes do not highlight any corrosivity trend.

Run	ID	Gasoline	Composition	Resistance increase (Ω/hrs)
6	S70	E0	Ethanol 0%	$1.12 E^{-3}$
6	S55	E10	Ethanol 10%	$8.48 E^{-4}$
6	S80	E20	Ethanol 20%	$4.37 E^{-3}$
6	S36	E100	Ethanol 100%	$2.32 E^{-3}$
7	S67	A20	Methanol 15% Ethanol 5%	$7.88 E^{-5}$
3	S23	M100	Methanol 100%	$-4.63 E^{-4} \approx 0$
3	-	E20 ref	Ethanol 20%	$-2.83 E^{-4} \approx 0$
6	-	E20 ref	Ethanol 20%	$-5.95 E^{-4} \approx 0$
-	-	-	-	-

Outcomes

- Despite the sensitivity of the Metallic Wire Resistance Method, the study highlighted that the method is not able to discriminate among the corrosivity of gasolines on Stainless Steel (304 / 430).

- A limited response of the system was observed for Copper. In this case, the Metallic Wire Resistance Method was able to identify the following corrosivity trend: E0 < E20 / E10 < A20 < E100 << M100.

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50 YEARS