High Sensitiity ER Sensor to Detect Metal Release and Film Forming in Oils and Lubricants on Copper

FEATURES

- Ratio-metric electrical resistance alternative to **"ASTM D 130/ 4048, IP 154"** Copper Strip Testing.
- Very high sensitivity to metal release and film forming. <0.03nm if used with **FMRT01** Transmitter.
- Surface can be cleaned and polished prior to exposure for multiple exposure tests.
- Large exposed surface 240mm2.
- Sealed edges to eliminate edge effects.
- No seed metal below Cu.
- High permanent operating temperature of 120°C.
- Easy additional optical examination after exposure tests.
- Bottom side of sensor substrate can be used as a coupon.
- Sensors are available in electro deposited or cold rolled Cu foil.

APPLICATIONS

- **Transformer Oil Monitoring and Testing.**
- **Engine Oil Monitoring and Testing.**
- **Grease Testing.**
- **Fuel Storage Monitoring.**
- **Oil for Life Testing in E-Drives.**
- **Nuclear Repository and Waste Storage. Container Monitoring and Testing.**
- **Cooling Water Monitoring for Generators.**
- **Laboratory Corrosion Testing on Cu.**


FMRS06 bottom view.
Can be used as a coupon.


FMRS06 top view

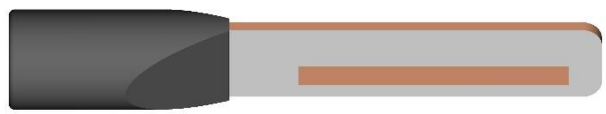

FMRS06 with epoxy foam header

For other headers, cables and connectors please contact SOLENICS

DESCRIPTION

To realize a highly sensitive and precise metal release test method, a quantitative-based copper thin-foil technology was developed. The thin-foil copper strips generate resistance values relative to the level of the medium corrosiveness. This thin-foil technology based sacrificial copper strips serve as a reliable sensor to track the progression of metal release, especially the corrosive by-products that are generated due to degradation (ageing) of oils, lubricants and fuels at elevated operating temperature. Solely detecting sulfur compounds (i.e., mercaptans, elemental sulfur, and organic sulfides) which can induce sulfur corrosion cannot provide enough information about the corrosiveness of the medium because other elements like water, acidic oxidation products and dissolved gases might also be present.

The proposed ratio metric electrical resistance sensor is comprised of two copper strips on a 2mm copper substrate. The reference element in plain with the exposed element and other areas which are not directly exposed to the test environment are masked off with a sulfur free white high temperature epoxy mask.
The two elements are connected in series and the resistance ratio is measured in 4 wire Kelvin connection in a modified Wheatstone Bridge arrangement where one bridge leg is the sensor and the second bridge leg is replaced by two subtractors in the instrument.
In combination with the FMRT01 instrument, resistance changes of <36nΩ for FMRS06 are detected. The ratio metric arrangement compensates for the temperature dependent electrical resistance in the element material provided the two elements are at the same temperature. For Cu a temperature difference of 0.001°C between the two elements generates an offset of ∼1 RRU (Resistance Ratio Units) if used with FMRT01.
Special attention was given to substantially minimize sensitivities to error signals like temperature gradients, strain, TCR offsets and differences in element resistivity between the two sensing elements.



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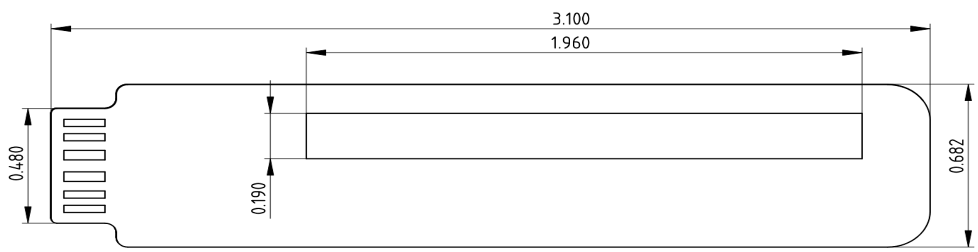
FMRS06 Copper Sensor Specifications

Header	High temperature closed pore Epoxy foam	For other headers please contact SOLENICS
Cable Coat Material	FEP over molded with header or sensor shaft	For other connections please contact SOLENICS
Sensor Substrate	Copper	
Metallization	Copper	Electro deposited or cold rolled foil
Coating (Mask)	Sulfur free high temp. Epoxy	
Total Cu Element Thickness	17.5µm	FMRS06 For other element thicknesses please contact SOLENICS
Effective Element Working Thickness	4.4µm	FMRS06 with FMRT01 setup for 1/4 span
Element Bulk Resistance	9.4 mΩ	FMRS06
Smallest Detectable Resistance Change	~36 nΩ for FMRS06	If used with SOLENICS Instrument FMRT01
Smallest Detectable Thickness Change	~0.03nm*	FMRS06
Exposed Element Surface Area	240mm^2	FMRS06
Permanent Operating Temperature Range	-20ºC to 120 ºC	Maximum operating temperature depends also on type of other materials used for packaging.
Excitation Method (Recommended)	15 to 30 Hz Sine Wave	
Excitation Current for FMRS06 (Recommended)	80mA to 120mA	A temperature increase of 0.001ºC through self-heating would occur at ~180mA for FMRS06.

*Thickness is not a measured value and is calculated out of the element resistance increase.
Calculated thickness can be below the thickness of a monolayer of material because the resistance of the element changes if only part of the surface is affected by metal release or conversion.
Resistance increase is also not linear over the decreasing cross section and doubles its value if half of the element cross section is lost or converted to something much less conductive than copper like Cu2O, CuO, Cu2S. See also explanation below.



Dimensions are in inches

Thickness versus Resistance for the FMRS06 Sensor or other Thin Walled ER Sensors

The electrical resistance method of metal release sensing is based on the increase in the electrical resistance of a conductor due to the reduction of cross section (thickness) as metal release or a conversion of the metal surface layers into another less conductive material takes place. This resistance of a conductor is decribed by:

$$R = \frac{\rho\, l}{A} \quad (1)$$

Above expession **(1)** holds only for round straight bulk conductors with a uniform surface and current density and non-swiched DC excitation. For thin metal strip conductors with grain sizes close or equal to the thickness of the conductor, grain size, grain structure and distribution affect the resistivity and the TCR (Thermal Coefficient of Resistance) of the conductor over thickness change. For metal films and thin foils the resistivity of the conductor changes over decreasing thickness approximately according to expression **(2)** and can be significantly higher for thin films below 500nm thickness.

$$\rho_d = \rho\left(1 + \frac{C}{d}\right) \quad (2)$$

where ρ is the conductors bulk resistivity, d is the conductors thickness and C is the electron scatter constant for the conductor material. Electron scatter occurs along the grain wall boundaies in the conductor and at the surface of the conductor. Grain size and structure affect the resistivity and the TCR of the conductor.

In a ratio-metric configuration with two thin rectangular conductor elements in close proximity (as used for FMRS06) and with one element changing its geometry (thickness) above expression **(1)** for R is a close approximation to describe resistance versus element thickness, but is not accurate and therefore not used to calculate metal release from resistance increase for the FMRS06 sensor.

For AC driven electrical resistance sensors as used here with the FMRT01 transmitter in ratio-metric configuration there are also other parameters which affect the theoretical (parabolic) non linearity of resistance versus cross section change as expressed by equation **(1).** These parameters are excitation frequency (proximity effect), element geometry, uneven current distribution, increasing surface roughness and decreasing thickness (increases current density in the exposed sensing element). Measurements have shown that the resistivity for the sensing element increases gradually as it gets thinner compared to the hidden reference element where all parameters remain unchanged. This gradual increase in resistivity over decreasing thickness minimizes the theoretical non linearity as it is expected from expression **(1)** for sensors here and elswhere.

Linearizing ER sensor response accordingly to expression **(1)** does therefore in most cases not improve the linearity of the ER sensor response. The ER sensor response can be linearized if the reistance can be related to a known element thickness. Linearization accordingly to expression **(1)** would magnify error signals like a difference in the temperature for the sensor elements (gradient) and in most cases overcompensate for the non linearity. It is therefore assumed that resistance change versus thickness has a linear relationship within the sensors working span. The working span (thickness) used for a FMRS06 sensor is 1/4 of the total thickness of the sensor element. The theoretical response curve shown in **Fig 1** is typical for all ER sensors with the same effective working span and is given for 1/4 and 1/2 span in **Fig. 1.**

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The actual sensor response varies depending on the conductor's thickness and geometry as outlined above and has for most geometries less than half of the none linearity for 1/4 and 1/2 span as shown in **Fig. 1**.

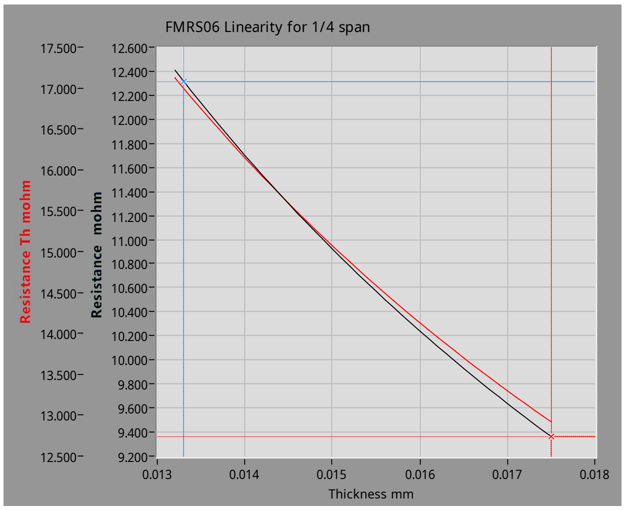
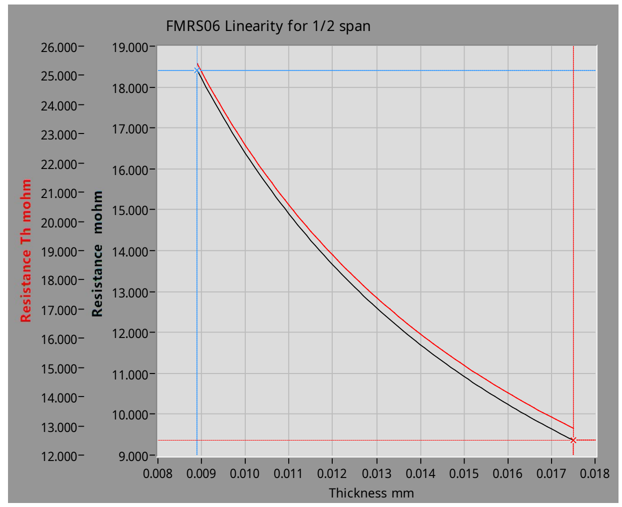


Fig. 1



FMRS06 Sensor Linearity for 1/4 and 1/2 Span.
Black Line: R at 20°C   Red Line: R at 120°C

The effective working span for the sensor if used with the FMRT01 transmitter is divided by the instruments resolution into 262144 resistance ratio units for a 1/2 span and 131072 resistance ratio units for a 1/4 span. For the FMRS06 element with a 1/4 effective working span the smallest detectable resistance increase is 36nΩ which accounts for a calculated average thickness decrease over the sensors surface of ∼ 0.03 nm. To achieve surface cleaning prior to exposure and and a reproducible relationship between element resistance and thickness the bulk element thickness for the sensor element is kept as thick as possible. The resistance of the sensing element increases by 1 ratio unit (RRU) if only 1/10 of the sensors surface releases 1 monolayer of Cu (∼ 0.3 nm).
It shall be noted, that a metal release of 10nm from a clean Cu surface at ambient temperature during a short exposure duration of 1 day represents in practice a significant amount of Cu release if exposed to oils fuels or lubricants. Therefore, only a small amount of the sensors span is used for a single exposure test and thickness calculations per test run are usually not performed over more than 50nm out of a total span of ∼ 4000 nm.

Metal Release Sensor FMRS06 versus ASTM D130 or ASTM D4048

The ASTM D130 copper strip test is designed to assess the relative degree of corrosivity of a petroleum product due to active sulfur compounds. The copper strip corrosion test is a widely used oil test method for gearbox, turbine and hydraulic lubricants. This oil test methode detects the corrosive effects of contaminents in oils, fuels and lubricants on copper and copper alloys.
The ASTM D130 copper strip test method is relative simple. A prepared copper strip is totally immersed in a sample of grease or oil and heated in an oven or liquid bath at a specified temperature for a definite period of time. The grease or oil sample is held in 50ml borosilicate glass cylinders.

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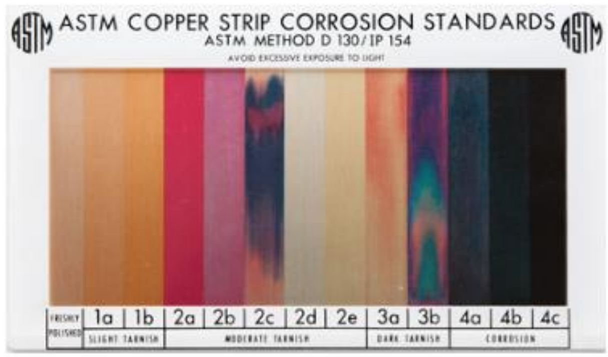
Test periods rang from hours to days and at the end of the heating period, the copper strip is washed and examined for evidence of tarnish. Results are rated comparing the stains on the copper strip to the ASTM color-match scale from 1A to 4C as shown below.



The ASTM D130 copper strip tarnish test method cannot provide information about the total metal release of the exposed metal strip. It can also not detect if tarnish formed on the copper surface was partially or completely dissolved by acidic ageing products in the product sample.

If the total metal release caused by the product sample is required, the electronic copper strip in form of a FMRS06 sensor can provide accurate information about the corrosivity of new or aged oils and lubricants. Additionally, the FMRS06 sensors copper bottom side allows for visual examination accordingly to ASTM D130 after exposure. The FMRS06 sensors can be used for short duration tests or long term permanent online monitoring.

Copper Corrosion and Dissolution

Several different types of chemical and electrochemical processes leadig to copper dissolution exist:

1) **Oxidative processes.**

$$4Cu + O_2 \rightarrow 2Cu_2O$$
$$Cu + ROO^{\bullet} \rightarrow Cu^{+} + ROO^{-}$$

2) **Reaction with acids in the presence of complexing agents or under oxidizing conditions.**

$$Cu + H^{+} + L \rightarrow CuL^{+} + 1/2H_2$$
$$2Cu + 2H^{+} + [O] \rightarrow 2Cu^{+} + H_2O$$

where [L] denotes a chelating ligand, and [O] denotes an oxidant (it may be hydroperoxide, peroxyacid, oxygen, etc).

3) **Reactions with corrosive sulfur compounds.**

$$2Cu + S \rightarrow Cu_2S$$

Heat produced during high-load operation of combustion engines or oil-filled transformers leads to accelerated oxidation of the lubricant or coolant. Ageing product accumulate in the oil and lead to higher metal release on copper or other metals.

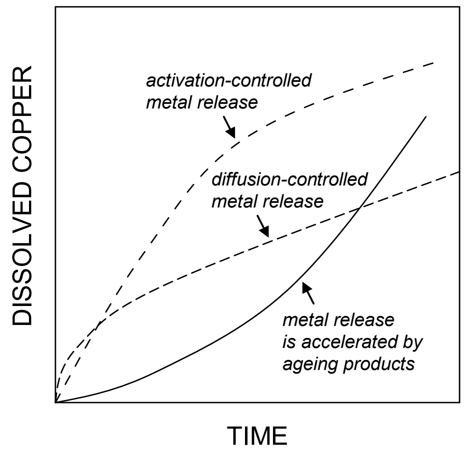


Fig. 2 Characteristic Copper Release Curves for Various Kinetic Scenarios

The relative importance of those processes varies greatly depending on the operational conditions, the base oil quality and the additive package. For instance, in highly loaded or overloaded transformers, operated at a high temperature, the thermal degradation of the insulating paper is unavoidable, no matter which oil and additives are used. In normally loaded open breathing transformer, oil oxidation will occur. In oil cooled transformers acidic oil oxidation products accumulating in oil not only affect the dissipation factor and insulating capability of the oil itself but also promote depolymerization of cellulose (insulation paper) and etch copper (wires) and other metal components.

Copper release kinetics as shown in **Fig. 2** are strongly influenced by oil quality, additives and ageing conditions. The mixed diffusion-activation controlled kinetic mechanism is applicable in most cases. Use of appropriate antioxidants, preverably in combination with a metal inhibitor, allows one to effectively minimize copper dissolution, specifically in open-vial experiments and in corrosive environments. The presence of dissolved water in oil slightly accelerates copper release. Free water in form of an emulsion can accelerate copper release significantly.

Metal release data shown below are generated from new and used motor oil and a new paraffinic transformer oil.

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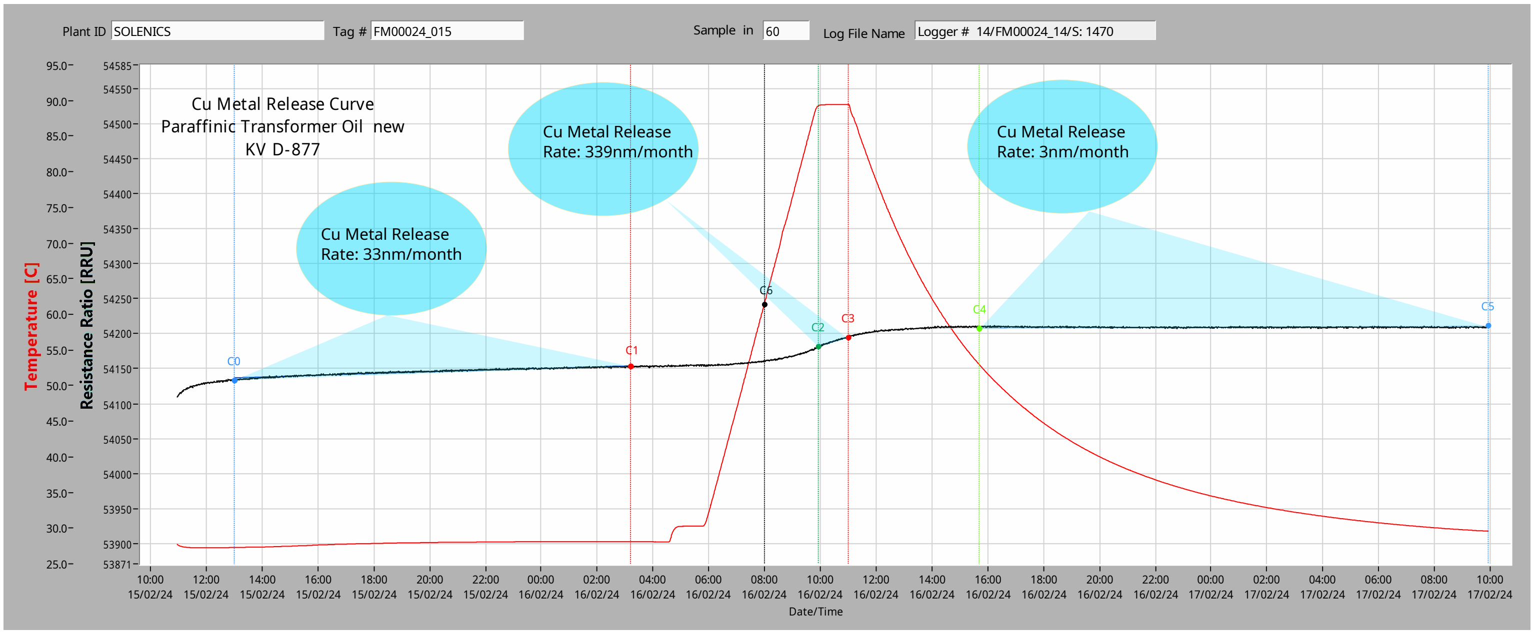
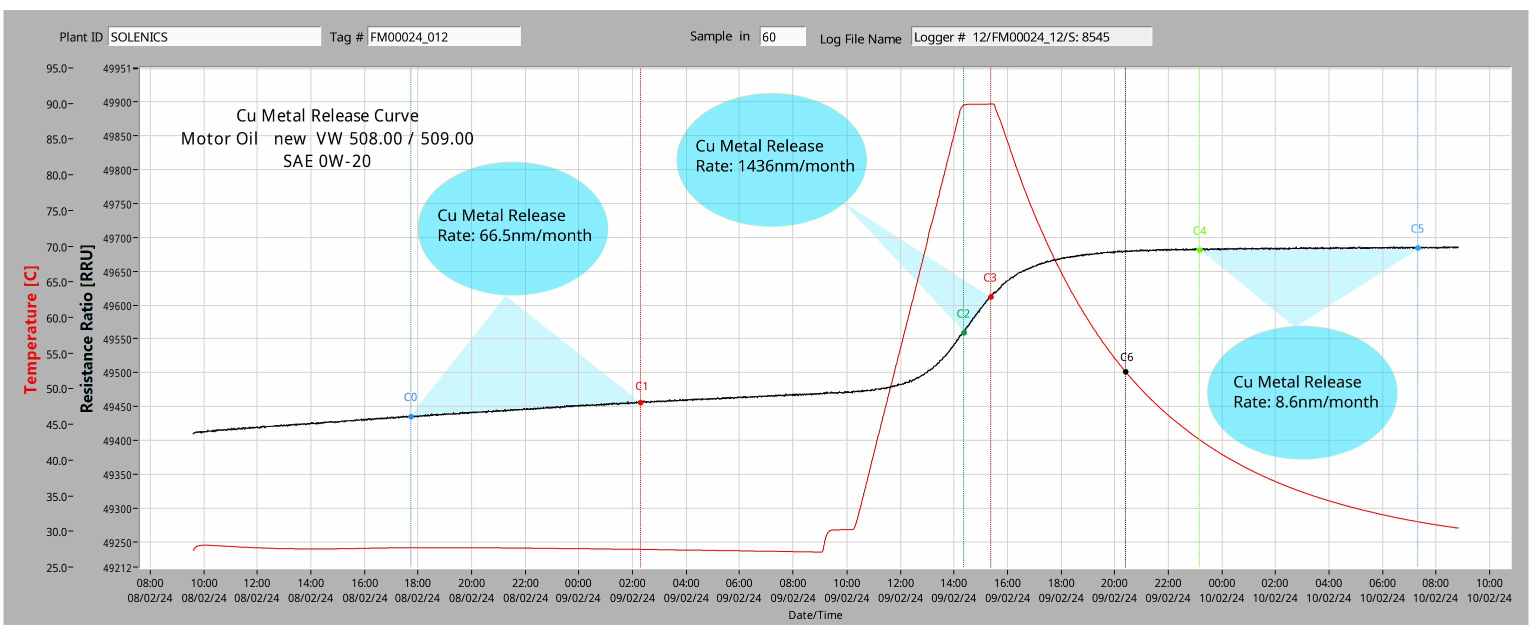
Cu Metal Release Curve for New Paraffinic Transformer Oil



Cu Metal Release Curve for New Motor Oil



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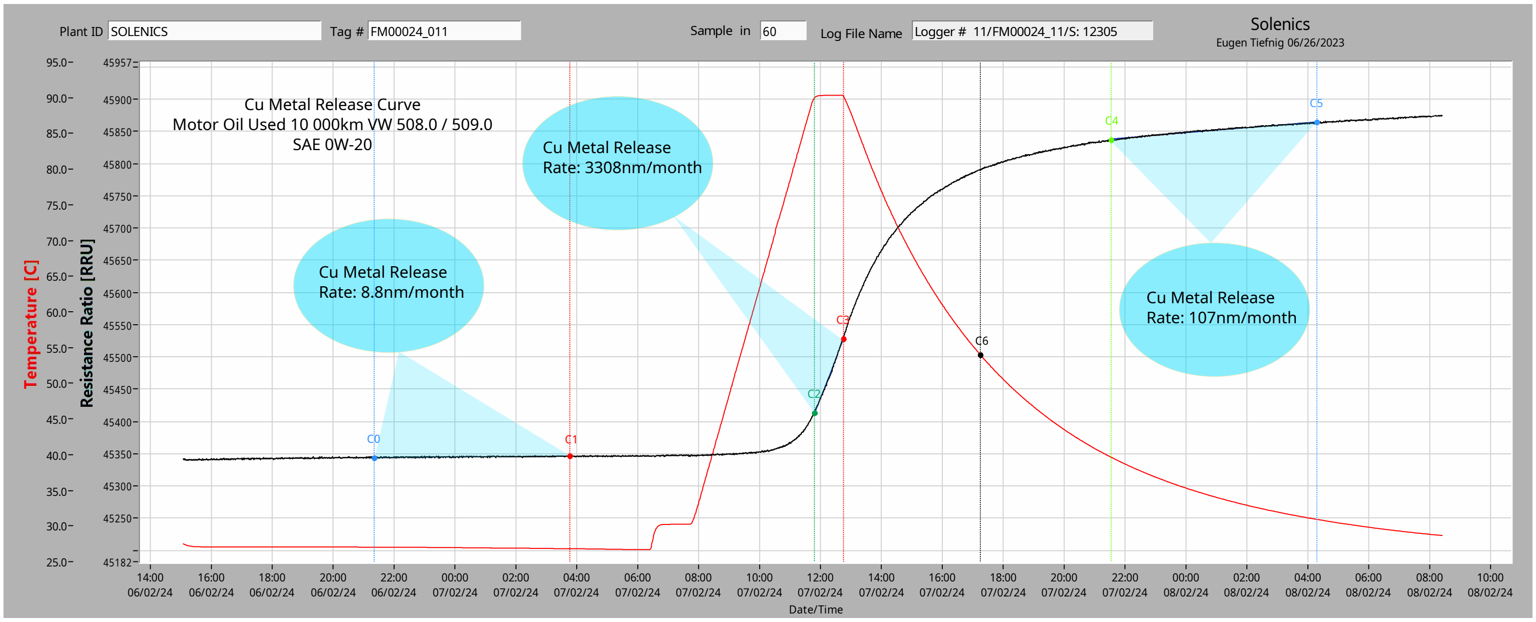
Cu Metal Release Curve for Motor Oil used for 10 000km



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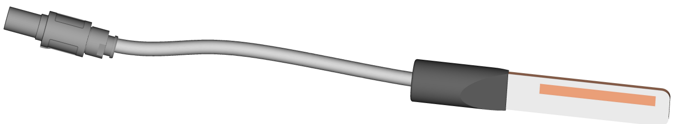
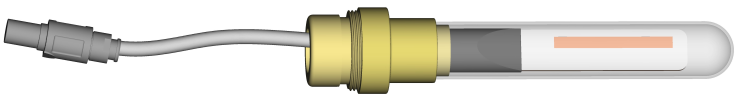
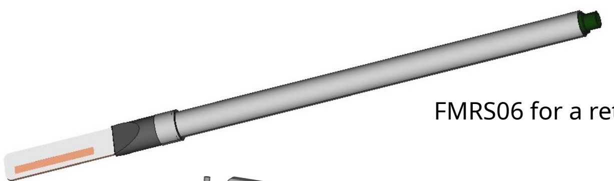
FMRS06 Sensor Assemblies for Laboratory and Online Applications



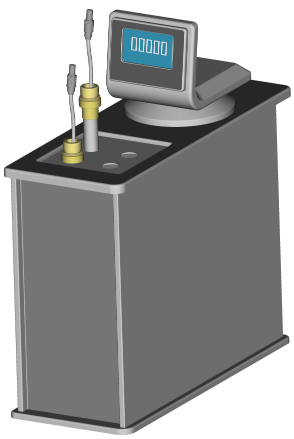
FMRS06 plain for atmospheric testing.



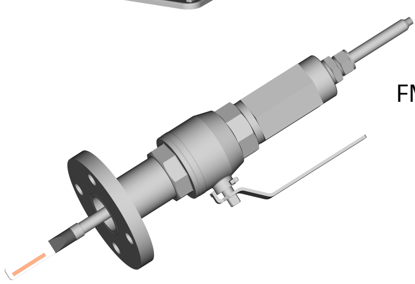
FMRS06 in Borosilicate glass tube



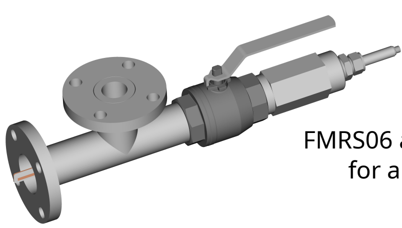
FMRS06 for a retractable fitting



FMRS06 in Borosilicate glass tubes inserted into a
recirculating liquid temperature bath



FMRS06 assembly in retractable fitting
for direct insertion into a vessel.



FMRS06 assembly in retractable fitting
for a flow through application.

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Notes: