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HYDRANAL™ Technical Information Sheet T013 Rev. 4

How to use Hydranal NEXTGEN Coulomat A-FA + C-FA reagents

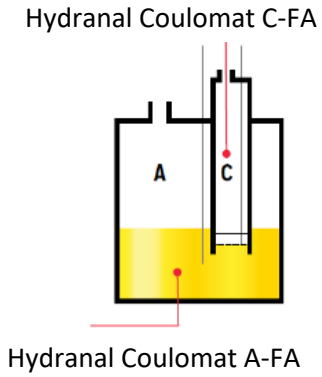
1. Appearance of the reagent

Color
Alcohol containing KF reagents are generally colorless or yellow. In contrast to this alcohol-free Coulomat A-FA and C-FA have a yellow-orange to deep orange color.

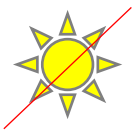
Coulomat AG | Coulomat AK | Coulomat A-FA

2. Filling the titration cell with diaphragm

Caution: FA reagents are very hygroscopic.
Fill and close the titration vessel and A-FA bottle as fast as possible to avoid water uptake.



1. Use a clear and dry titration vessel and generator electrode. Ideal conditions: Vessel and especially the generator electrode dried at 50°C overnight.
2. Before connecting the indication electrode to the vessel: Clean the platinum pins gently with a soft paper tissue.
3. Snap off top tag of the Coulomat C-FA ampoule at the predetermined breaking zone.
4. Transfer one ampule of C-FA into the cathodic chamber (use a dry syringe or a funnel).
5. Fill the anode compartment with the anolyte Coulomat A-FA (use a dry funnel). The anolyte level should initially be a few millimeters higher than the catholyte level.
6. Before closing the titration vessel, dry contaminated glass parts with a paper tissue.
7. Start the conditioning mode and wait till drift is below 10 µg/min (ideally below 5 µg/min).
8. Speedup the conditioning phase:
   After receiving a drift value < 20 µg/min “shake” gently the titration cell and “wash” the titration cell wall with the anolyte. Avoid reagent contact with upper glass parts and sleeve junctions!



Recommendation:
Keep the reagent away from sunlight or artificial sunlight lamps.
When reagent is used in a colorless titration cell, auto iodine production may take place. The titrator may over titrate and/or drift values may drop to zero. If sunlight cannot be avoided, cover the titration cell with aluminum foil. Alternatively, brown-glass titration vessels are available from many equipment suppliers.

Store the reagent bottle under dry conditions in a dark place below 30°C.

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3. Can also a cell without diaphragm be used with FA reagents?

Yes	For ketones	Please consider that results will be increased by up to 10% if a cell without diaphragm is used
No	For LiB electrolytes and oils	Redox reactions can damage the cathodic platinum electrode (especially, if samples with highly reactive additives like FEC and VC are titrated)!

4. When should the anolyte and the catholyte be replaced?

1. At least once a week
2. If recovery of Hydranal Water Standard 0.1 PC is higher than +/- 10%
3. As soon as sample-related deposits are formed inside anode or cathode compartment. Solid deposits can damage the generator electrodes.
4. If the drift increases continuously above 20 µg/min

5. Which water standards can be used?

For verification of the titration cell, alcohol-free water standards are recommended:

Art. No.	Water Standard	Description	Matrix	Comment
34446	HYDRANAL-Water Standard 0.1 PC	Liquid standard, water content 0.1 mg/g = 0.01%	Propylene Carbonate	Highly recommended
34847	HYDRANAL-Water Standard 0.1	Liquid standard, water content 0.1 mg/g = 0.01%	Xylene	May decrease the solubility of LiB-electrolytes
34426	HYDRANAL-CRM Water Standard 1.0	Liquid standard, water content 1.0 mg/g = 0.1%	Anisole	Do not use with LiB electrolytes

Caution: Do not use water standards that contain alcohols

Even small amounts of alcohol destroy the alcohol-free system.
Strong side reactions with alcohol-sensitive samples will occur and incorrect titration results and/or high drift values will be obtained. For information on composition, please check the safety data sheet of each water standard used. Examples of non-compatible alcohols:

Methanol, ethanol, propanol, butanol, 1-methoxy-2-propanol / 1-Methoxypropan-2-ol

6. How to increase the solubility of LiB-electrolytes in FA reagents?

To increase the solubility of many lithium battery (LiB) electrolytes, we recommend adding 20-30% N-Methylformamide (NMF) to Coulomat A-FA in the anodic chamber of the titration cell.

Ensure that the NMF used is of high quality, with a purity greater than 99% and a water content ideally below 100 ppm. To further reduce the water content, store the NMF above a 2-3 cm layer of molecular sieve in its original bottle for 24 hours. After this period, it is recommended to decant the solvent into a clean brown glass bottle, as the long-term effects of the reactive silica surface on NMF quality are not fully understood.

Caution: Never add NMF directly to the original Coulomat A-FA reagent bottle. Over time, NMF will degrade the performance of FA reagents, leading to their decomposition into amines and other byproducts during storage. Always prepare the A-FA and NMF mixture freshly in the titration cell.

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7. Handling of water standards

1. Shake the ampoule
2. Snap off the top tag of the ampoule at the predetermined breaking zone
3. Rinse the needle and the plunger by taking approx. 0.5 mL standard into the syringe. Avoid taking any air into the syringe
4. Discard rinsing solution and wipe the needle dry. Do not pull plunger up and down to avoid taking any air into the syringe
5. Draw the rest of the standard immediately into the syringe. Leave a few drops in the ampoule.
6. Remove any possible air bubble from syringe and wipe the needle dry
7. Add an aliquot of standard (at least 1 mL) by back-weighing to the titration vessel and carry out the titration
8. Remove a few drops of standard from the tip of the syringe before further use and wipe the needle dry again
9. Repeat steps 7-8

8. Excess of iodine

water excess neutral iodine excess

Depending on the storage conditions, a reaction can be triggered, generating iodine production inside the original bottle. This can generate an excess of iodine in the reagent and cause the solution to become brown. If the titration cell is filled with such a darkened reagent, the titrator indicates an end-point parameter and is not able to start the conditioning mode. This can result in an error message indicating “over-titration” “check generator electrode” or “short circuit”.

If the A-FA reagent is brown (as opposed to the orange sample pictured above) an excess of iodine is present in the reagent. Excess of iodine does not have a negative impact on the product quality or render the reagent unusable.

An excess of iodine needs to be reduced by addition of water before use. Never use pure water directly! Use a water/co-solvent mixture as described below.
Add 1 mL of the mixture to the anodic compartment containing 100 mL Coulomat A-FA and start the the conditioning mode.

Preparation of water/co-solvent mixture:
Add 150 mg (0.15 mL) water to 50 mL of pure acetonitrile or liquid carbonate (PC, EC, EMC, DMC, etc.) and mix properly.

Caution: Never add carbonates to the A-FA reagent bottle. In long term carbonates will destroy the performance of FA reagents (decomposition to alcohols and other products during storage).

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9. Recommended Titration Parameter

Examples:

	Metrohm *Hydranal-Coulomat A-FA / C-FA* *for **li-battery electrolytes*** *Cell with diaphragm*	***Metrohm*** *Hydranal-Coulomat A-FA / C-FA* *for **ketones*** *Cell with diaphragm*
Max. rate	max. µg/min	max. µg/min
Min. rate	15 µg/min	15 µg/min
Extraction time	15 s	15 s
Stirring speed	8	8
Drift correction	auto	auto
Stop time	off	off
Stability time	**70 s**	**70 s**
Pause	0 s	0 s
Polarization current	10 µA	10 µA
Gen. current	auto mA	auto mA
Endpoint	50 mV	50 mV
Dynamics	70 mV	70 mV
Start drift	20 µg/min	**40 µg/min**
Rel. stop drift	5 µg/min	5 µg/min

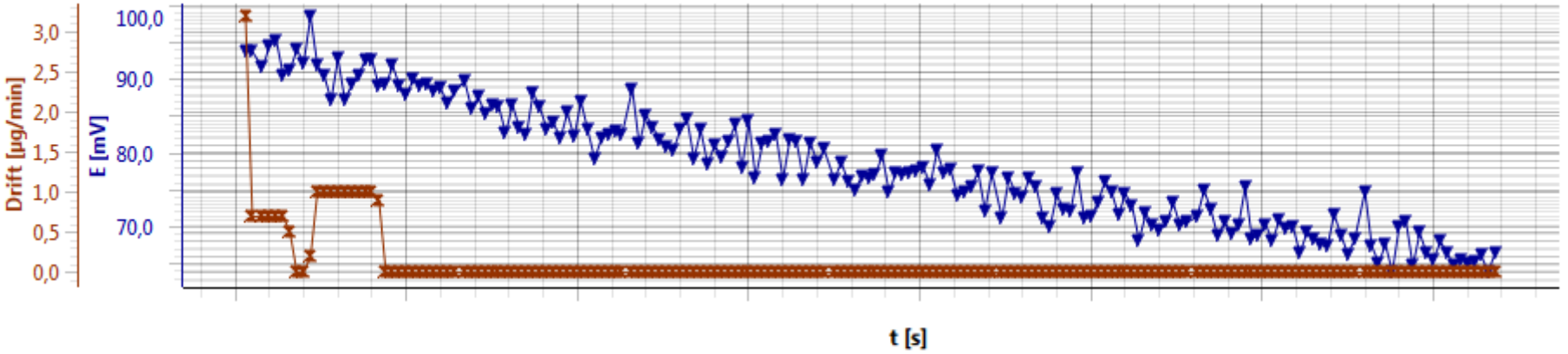
	Mettler Toledo *Method M882* *Water < 100 ppm* *Hydranal-Coulomat* *A-FA / C-FA for **li-battery electrolytes*** *Cell with diaphragm*	***Mettler Toledo*** *Hydranal-Coulomat* *A-FA / C-FA **for ketones*** *Cell with diaphragm*
Mixing time	**1 s**	**1 s**
Ipol	5.0 µA	5.0 µA
Start drift max.	20 µg/min	**40 µg/min**
Endpoint	100 mV	100 mV
Control band	**350 mV**	**180 mV**
Rate	Normal	Normal
Generator power	Auto	Auto
Drift stop relative	1 µg/min	1 µg/min
Min. time	**40 s**	**60 s**
Max. time	Infinity	Infinity
Stirring speed	60%	60%

For recommended titration parameter of other titration equipment like e.g. SI-Analytics, ECH, Mitsubishi, please contact us at hydranal@honeywell.com

UV-Light Induced Auto Iodine Production

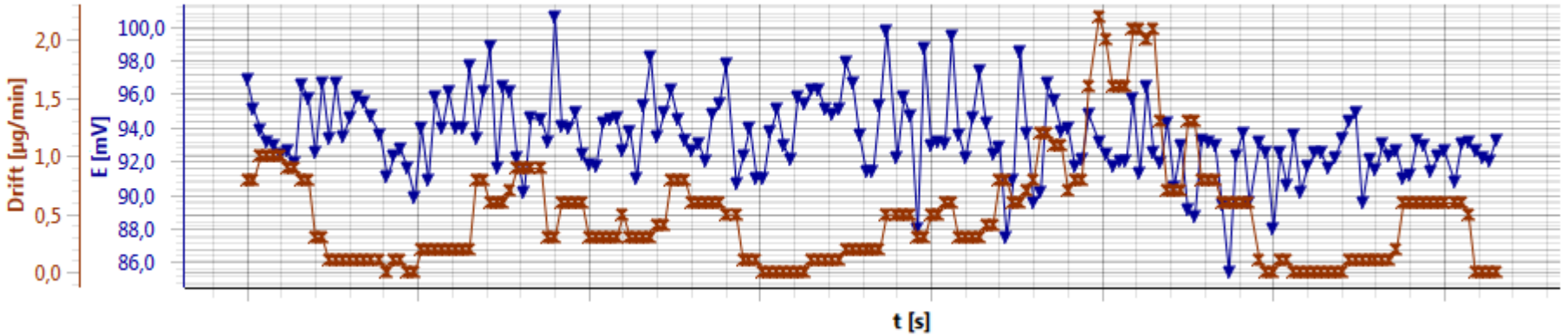
➔ During conditioning mode, the indicator current can reach values below endpoint parameters, <u>if the titration cell is exposed to UV-light</u>.
(e.g. E << 100 mV for Mettler Toledo; E << 50 mV for Metrohm)
As a result of that the drift stays at 0 µg/min and drift correction is not working properly anymore.

- Next titration would give an underdetermined result
- Please use an amber glass titration cell or a HYDRANAL™-UV-SHIELD (see page 2/3)
  - If you see a drift value that stays at 0 µg/min for more than one minute
  - If you see error message "over titrated"



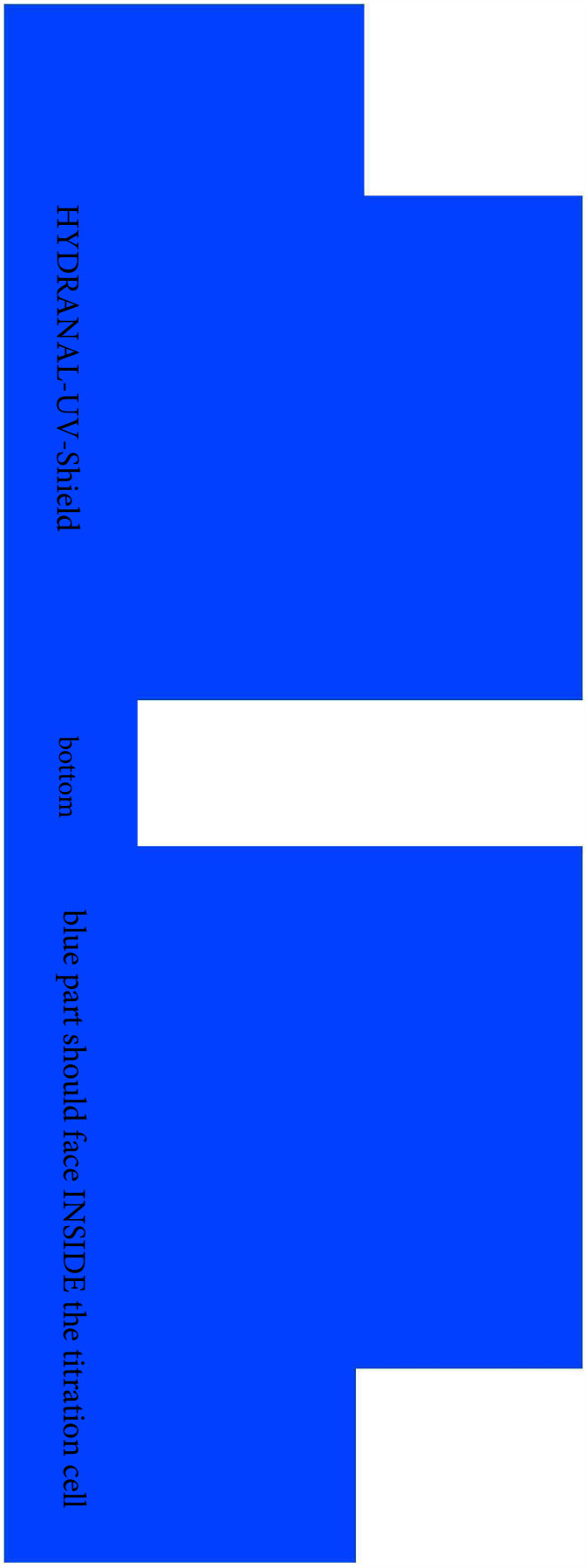
With Amber Glass Titration Cell or HYDRANAL™-UV-SHIELD:

➔ Stable conditioning, no over-titration

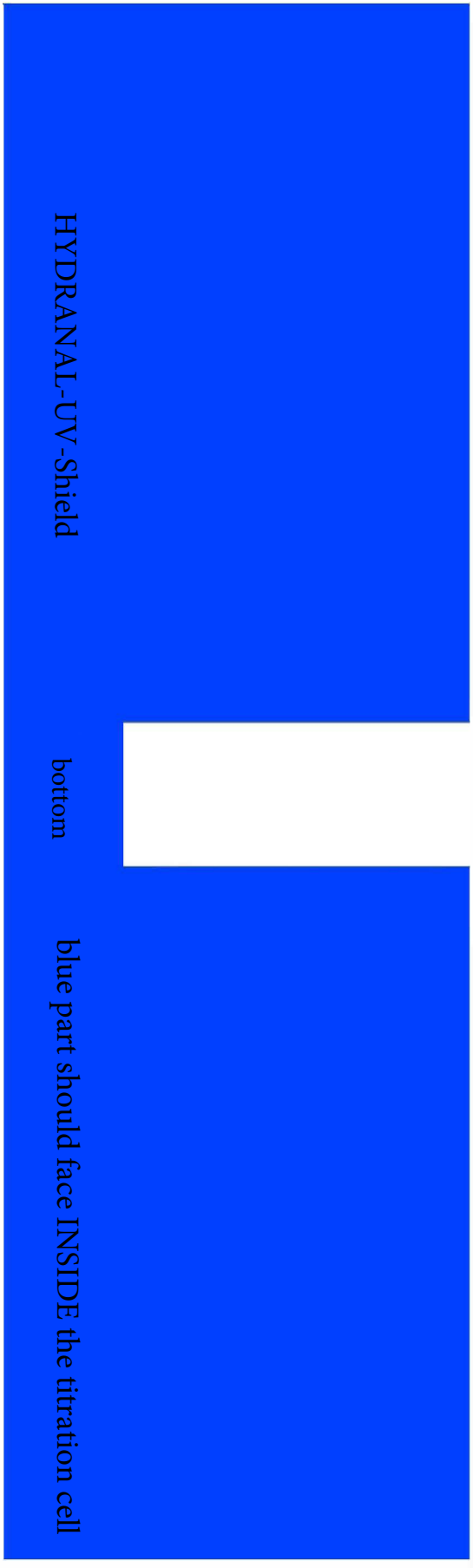


HYDRANAL™-UV-Shield Template for Light Sensitive KF-Reagents

Metrohm titration cell



Mettler-Toledo titration cell



1. Print out the template in color (A4 size). 2. Cut out the blue part of the template. 3. Wrap it around the titration cell (blue part should face inside). 4. Connect the long ends of the template with a duct tape.

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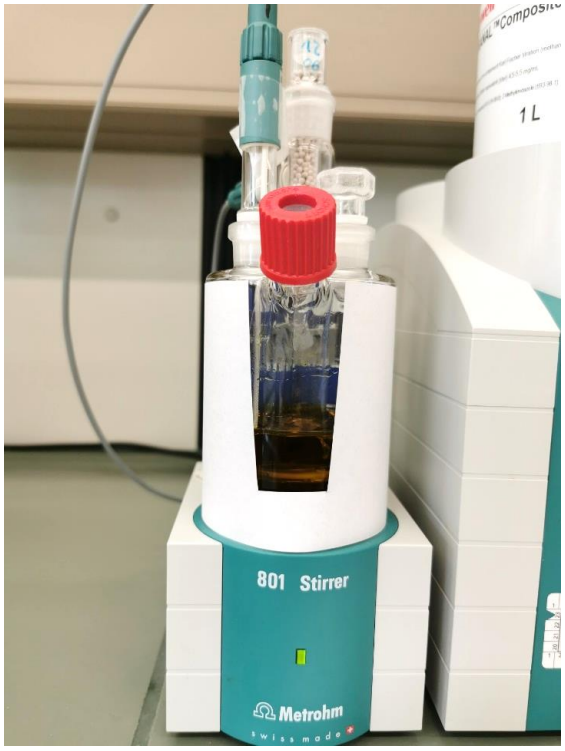
Examples of correct use of HYDRANAL™-UV-SHIELD:



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11. Further Information

https://lab.honeywell.com/en/hydranal/nextgen/fa-reagents

Articles and Whitepapers:

- ➔ Hydranal NEXTGEN FA for ketones Flyer
- ➔ Hydranal NEXTGEN FA for ketones Whitepaper
- ➔ Hydranal NEXTGEN FA for LiBs Flyer
- ➔ Hydranal NEXTGEN FA for LiBs Whitepaper

Technical information sheets:

- ➔ Recommended handling of water standards:
  See Hydranal-Technical Information Sheet T007

12. Products

Reagents and Water Standards:
34470 HYDRANAL-NEXTGEN Coulomat C-FA
34471 HYDRANAL-NEXTGEN Coulomat A-FA

34426 HYDRANAL-CRM Water Standard 1.0
34446 HYDRANAL-Water Standard 0.1 PC

Auxiliaries:
34881 Riedel-de Haën-Acetonitrile R CHROMASOLV™, ≥99.8% (GC)
34241 HYDRANAL-Molecular Sieve 0.3 nm
N-Methylformamide (>99%)

Hydranal Center of Excellence
Honeywell Research Chemicals
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