HYDRANAL™ NEXTGEN FA REAGENTS

WORLD'S FIRST COMMERCIALLY AVAILABLE KARL FISCHER TITRATION REAGENTS FREE OF ALCOHOL AND FREE OF IMIDAZOLE

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Honeywell

HYDRANAL NEXTGEN | NEW FA-TYPE!

New Hydranal FA (free of alcohols) reagents solve challenging LiB (lithium-ion battery), ketone and oil applications while keeping safer formulation

SMARTER TECHNOLOGIES

Upgrade to RFID technology that allows seamless data transfer from our reagents to your titrator.

Smart Chemicals for Mettler-Toledo (-SC)

Smart Reagents for Metrohm OMNIS (-OM)

SAFER FORMULATIONS

Our improved formulations promise the same global performance standard but without the CMR* risk.

Free of imidazole (FI)

SUPERIOR SOLUTIONS

We solve for new and challenging applications, creating solutions that give you the best results.

Free of imidazole (FI)

Free of alcohols (FA)

The Next Generation in Karl Fischer Titration is Here

*CMR = carcinogenic, mutagenic and reprotoxic

HYDRANAL NEXTGEN FA REAGENTS

Customer Problem

- LiB electrolytes with certain additives cannot be analyzed for water content due to side effects
- Some LiB electrolytes can be analyzed but reagent needs to be changed very frequently
- Currently special reagents for ketones (Coulomat AK + CG-K) and oils (Coulomat Oil + CG) contain imidazole (CMR substance) and toxic chloroform

Current Solution

- Some LiB electrolytes are not analyzed for water content. Only raw materials are tested → high performance - and **safety risk**
- Very frequent reagent exchange increases the **cost of analysis**
- Using reagents with CMR* classification requires **risk assessment studies** to be performed in the lab

New Solution with FA

- ✓ **Universal** reagent for many types of LiB electrolytes, ketone and oil samples; **high accuracy** of results
- ✓ Reagent needs to be changed less frequently than the one currently used (**lower cost** of analysis)
- ✓ New reagents are **safer**: free of imidazole (without CMR* classification) and free of toxic chloroform (no need for additional documentation)

Solving challenging applications

*CMR = carcinogenic, mutagenic and reprotoxic

WATER DETERMINATION IN LIB ELECTROLYTES

Humidity plays a dominant role in the quality and stability of batteries.

Most batteries require water-free electrolytes, because water can be electrolyzed to give H_2 and O_2 gases that can cause the battery to explode.

To ensure product quality and safety, low water content is one of the key requirements for LiBs.

To fulfill this requirement, the ability to perform highly accurate water determinations is critical.

TITRATION PROBLEMS WITH CURRENTLY AVAILABLE KF REAGENTS

- Alcohols undergo side reactions with the additives used in many LiB electrolytes.
- Difficult or even impossible to measure water content in most prominent LiB electrolytes that contain additives such as:
  - VC
  - FEC
  - Borates such as LiBOB and LiDFOB

Sample	Coulomat A-FA + C-FA	Coulomat AK + CG-K	Reagent M
LiB electrolyte with VC/FEC	+	o	o
LiB electrolyte with LiBOB	+	-	-
LiB electrolyte with LiDFOB	+	-	-
Pure VC	+	-	-
Pure FEC	+	o	o
Pure LiBOB	+	-	-
Pure LiDFOB	+	-	-
Ketones	+	+	-

\+ accurate titration, suppressed side effects
o limited titration (possible only for small amount of sample)
\- no accurate titration possible

VC = vinylene carbonate
FEC = fluoroethylene carbonate
LiBOB = lithium bis(oxalate)borate
LiDFOB = lithium difluoro(oxalato)borate

MECHANISM OF TITRATION

KF reaction mechanism in alcoholic media:

1. $CH_3OH + SO_2 + RN \leftrightarrow [RNH]SO_3CH_3$ (RN = base)
2. $H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4CH_3 + 2\ [RNH]I$ Stoichiometry $H_2O:I_2 = 1:1$

KF reaction mechanism in non-alcoholic media:

1. $SO_2 + I_2 + H_2O \rightarrow SO_3 + 2HI$
2. $SO_3 + H_2O \rightarrow H_2SO_4$ Stoichiometry $H_2O:I_2 = 2:1$

Proposed KF reaction mechanism in Hydranal‘s FA reagents:

1. $MeSO_3H + RN{\cdot}SO_2 \leftrightarrow [RNH]MeSO_3SO_2$ ($MeSO_3H$ = Methanesulfonic acid; patent pending)
2. $H_2O + I_2 + [RNH]MeSO_3SO_2 + 2\ RN \rightarrow [RNH]MeSO_3SO_3 + 2\ [RNH]I$ Stoichiometry $H_2O:I_2 = 1:1$

SIDE REACTIONS: UNSATURATED COMPOUNDS

Sample	As raw material	As additive	Comment
Unsaturated compounds (e.g. VC, vinyl acetate)	No or fading end point Accurate water determination is impossible.	Increasing drift. Decreasing accuracy of titration.	Iodine-consuming side reaction occurs.
FEC	Causes fewer problems compared to VC when sample size is small Otherwise, no or fading end point.	Causes fewer problems if the absolute water content in the sample is low.	Can be titrated with low water content in small portions; however, small sample size increases weighing error.

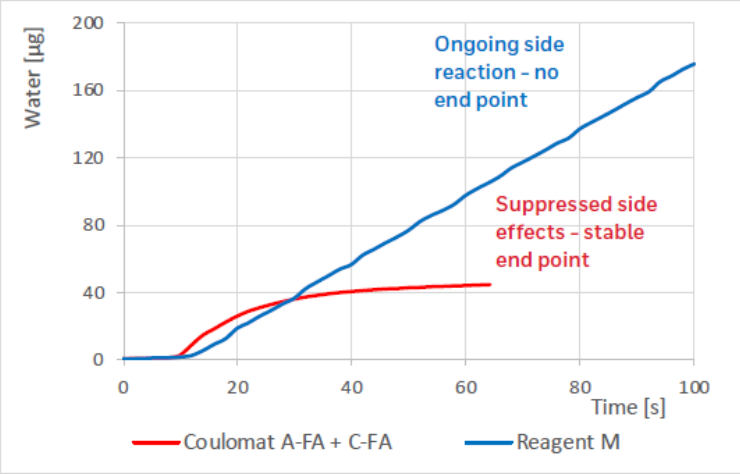
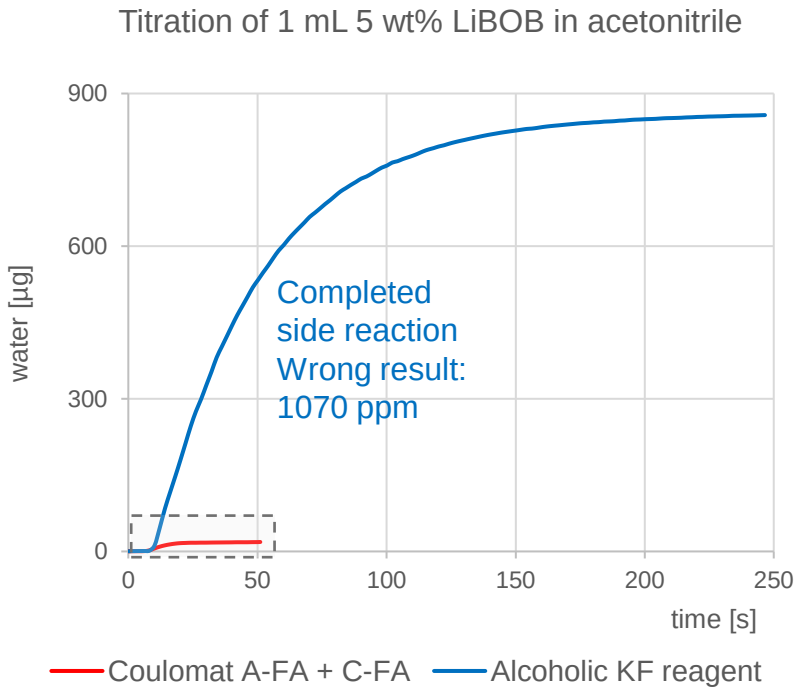


Fig. 2. Titration of pure VC.

SIDE REACTIONS: BORATES

Sample	As raw material	As additive	Comment
Borates (e.g. LiBOB, LiDFOB)	Accurate water determination is impossible.	Long titration with highly overdetermined results. Note: end point can be reached, but giving incorrect result	Water-releasing side reaction occurs.



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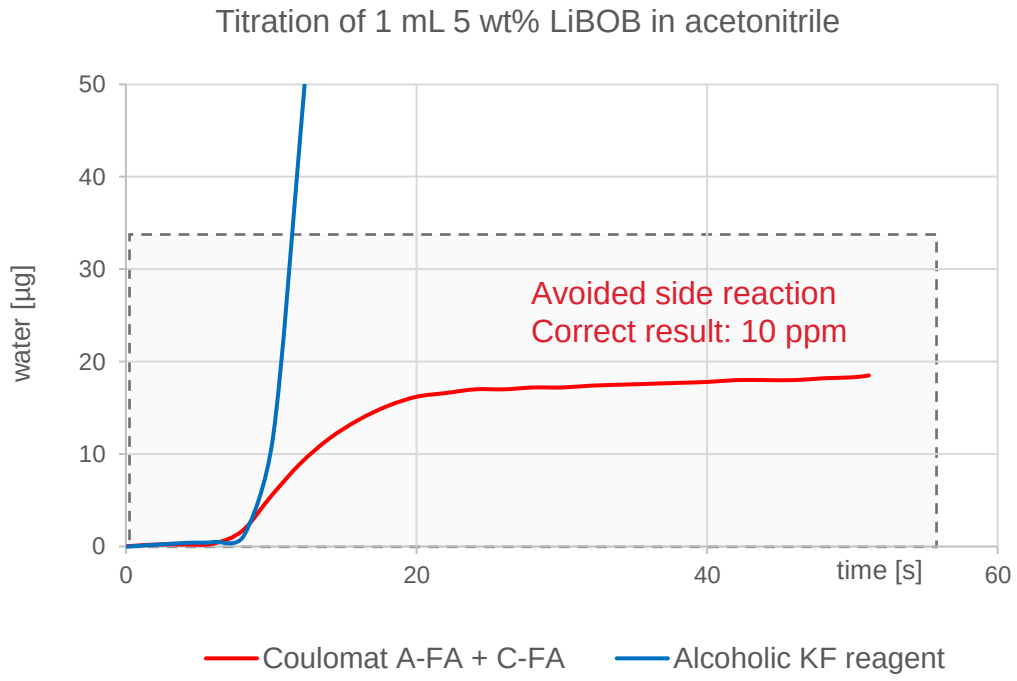
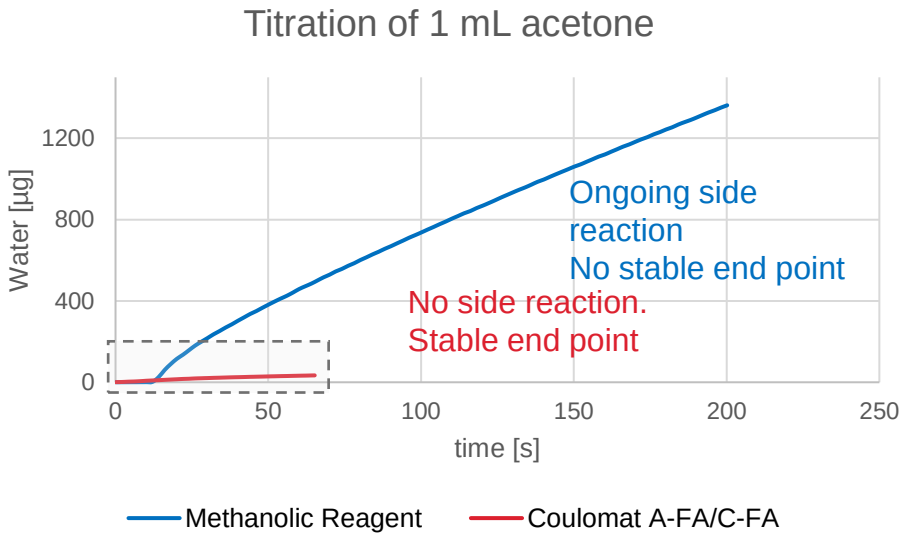


SIDE REACTIONS: KETONES

Sample	As raw material	As additive	Comment
Ketones (e.g. acetone)	No or fading end point. Accurate water determination is impossible.	Long titration with highly overestimated results. No or fading end point. Increasing drift.	Water-releasing side reaction occurs. Acetone and diketones are decomposition products in LiB electrolytes containing propylene carbonate (PC).



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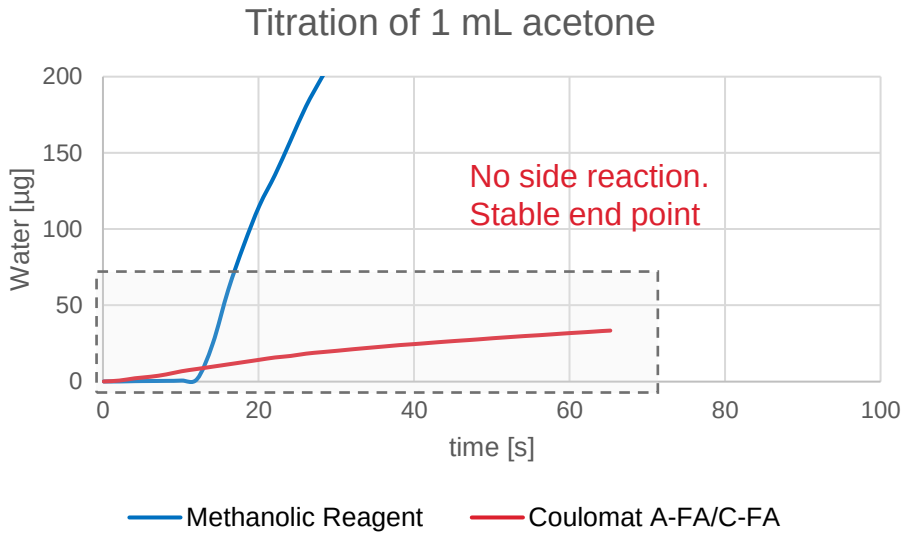
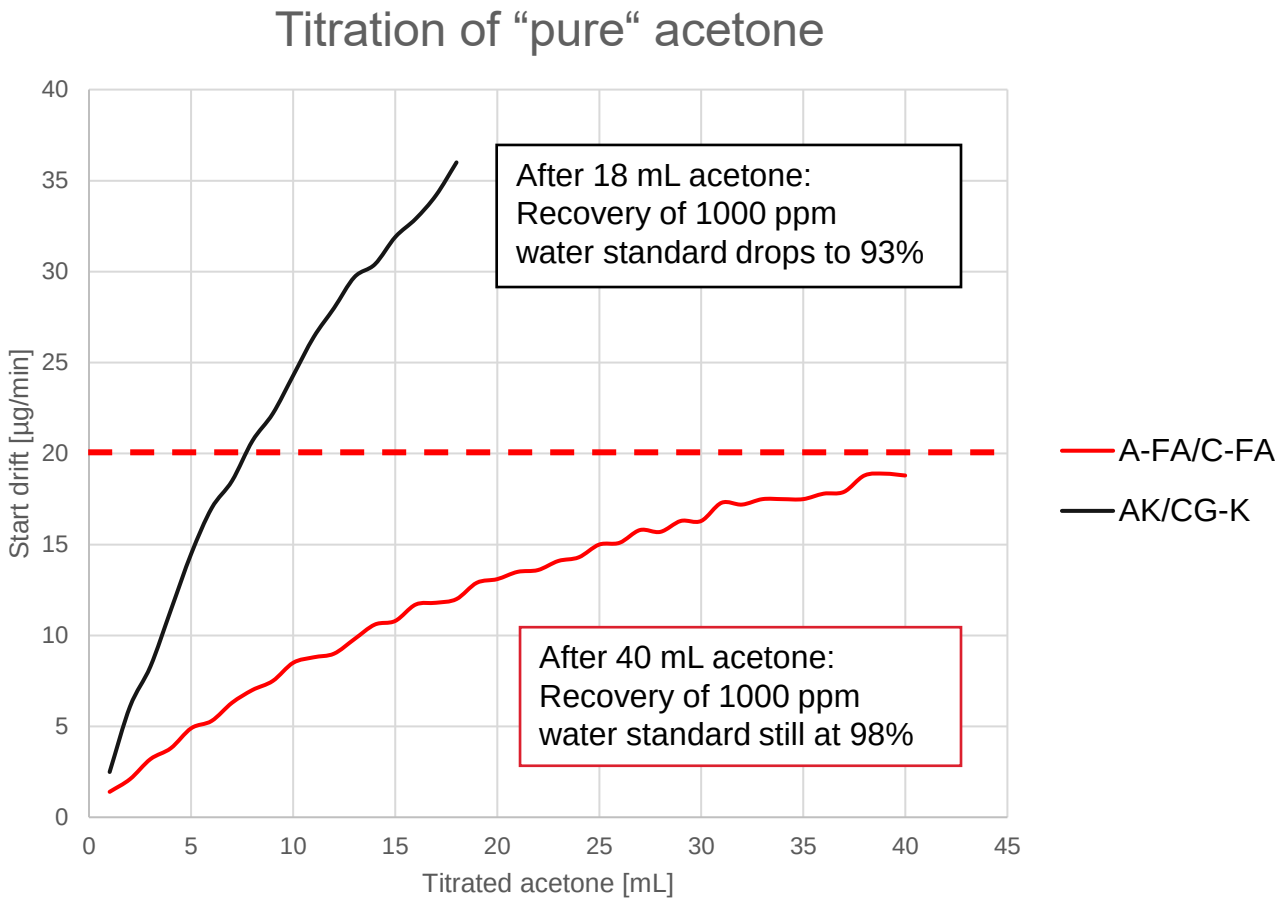


SIDE REACTIONS: KETONES
ADVANTAGE OF A-FA / C-FA



Coulomat A-FA/C-FA -> methanol-free; without alcohols

Coulomat AK/CG-K -> methanol-free; with alcohol derivatives

- When using Coulomat AK/CG-K, the start drift increases above 20 µg/min after the titration of approx. 8 mL of “pure” acetone
- when Hydranal NEXTGEN Coulomat FA reagents are used, the start drift keeps below 20 µg/min even after the titration of 40 mL of “pure” acetone.
- The recovery of 1000 ppm water stays at 98%, whereas the recovery of Coulomat AK/CG-K already drops to 93% after the titration of 18 mL of “pure” acetone

“Pure” acetone is free of decomposition products, while “impure” acetone is mostly contaminated with methyl ethyl ketone, methyl isobutyl ketone, and higher acetone condensation products (self-decomposition of acetone). “Impure” acetone has a significantly stronger negative effect on drift increase and recovery.

TITRATION EXAMPLES

Sample	Mean water content (n = 4-6) [ppm]	Abs. std. dev. [ppm]
Lithium salts		
Lithium acetate	102.3	1.9
Lithium bis(oxalato)borate (LiBOB)[1] (over molecular sieves)	10.0	0.2
Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)[1]	13.7	4.2
Lithium difluoro(oxalato)borate (LiDFOB)[1]	77.4	0.7
Lithium nonafluoro-1-butanesulfonate[1]	4.3	2.4
Carbonates		
Fluoroethylene carbonate (FEC)	33.1	0.2
Propylene carbonate (PC)	98.8	0.5
Vinylene carbonate (VC)	88.2	0.1
Sulfurous compounds		
Allyl methyl sulfone	1571.4	20.4
Ethylene sulfite	466.5	0.9
Ethylene sulfite (over molecular sieves)	27.3	0.1
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	694.4	2.9
1,3-Propanesultone[1]	31.7	0.2
2-Propynyl methanesulfonate	575.2	5.7

Sample	Mean water content (n = 4-6) [ppm]	Abs. std. dev. [ppm]
Ketones		
Acetone (over molecular sieves)	7.2	0.5
Acetylacetone	561.9	1.1
2-Butanone (over molecular sieves)	6.3	0.5
Methyl acetoacetate	27.6	0.6
Methyl levulinate	71.4	0.5
4-Methy-2-pentanone	188.9	0.2
Other		
Acetonitrile	8.2	0.2
Adiponitrile	13638.8	73.9
Allyl acetate	368.1	3.7
Tert-Amylbenzene	124.3	0.2
Phenylcyclohexane	95.8	0.2
Tris(trimethylsilyl) borate	Not possible	
Tris(trimethylsilyl) phosphite	Not possible	
Vinyl acetate	56.8	0.4

[1] 5 wt% in acetonitrile

TITRATION EXAMPLES

Successive titrations of LiB additives in one vessel filling with 100 mL Hydranal NEXTGEN Coulomat A-FA and 5 mL Hydranal NEXTGEN Coulomat C-FA.

No.	Sample	Water measured [ppm]	Water measured [µg]	Titration time [s]	Start drift [µg/min]	Water recovery [%]
1	**1 mL water standard 102 ppm**	**105.3**	**127.8**	**55**	**4.3**	**103**
2	1 mL VC	88.1	115.9	59	4.2	
3	1 mL VC	88.4	120.3	55	4.9	
4	1 mL VC	88.2	119.9	55	5.2	
5	1 mL VC	88.3	118.6	59	5.1	
6	1 mL VC	88.2	114.2	55	5.7	
7	**1 mL water standard 102 ppm**	**105.0**	**126.4**	**58**	**5.9**	**103**
8	1 mL FEC	32.9	46.6	56	3.1	
9	1 mL FEC	33.2	49.6	53	3.1	
10	1 mL FEC	33.4	50.3	56	3.1	
11	1 mL FEC	33.0	48.7	56	3.3	
12	1 mL FEC	33.1	47.3	57	3.3	
13	**1 mL water standard 102 ppm**	**104.4**	**126.9**	**59**	**3.2**	**102**
14	1 mL 2-Propynyl methanesulfonate	566.4	698.4	81	3.0	
15	1 mL 2-Propynyl methanesulfonate	570.5	720.7	80	3.8	
16	0.5 mL 2-Propynyl methanesulfonate	576.8	374.3	72	4.7	
17	0.5 mL 2-Propynyl methanesulfonate	577.1	371.2	69	4.7	
18	0.5 mL 2-Propynyl methanesulfonate	578.3	366.4	66	4.7	
19	0.5 mL 2-Propynyl methanesulfonate	582.0	350.1	66	4.4	
20	**1 mL water standard 102 ppm**	**98.9**	**120.4**	**63**	**4.7**	**97**

EXAMPLES

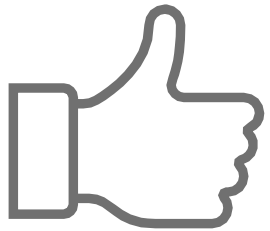
Successive titrations of LiB additives in one vessel filling with 100 mL Hydranal NEXTGEN Coulomat A-FA and 5 mL Hydranal NEXTGEN Coulomat C-FA.

No.	Sample	Water measured [ppm]	Water measured [µg]	Titration time [s]	Start drift [µg/min]	Water recovery [%]
1-19						
20	**1 mL water standard 102 ppm**	**98.9**	**120.4**	**63**	**4.7**	**97**
21	1 mL Allyl methyl sulfone	1535.5	1848.2	113	4.5	
22	0.5 mL Allyl methyl sulfone	1575.0	939.9	86	6.2	
23	0.5 mL Allyl methyl sulfone	1579.6	925.0	87	6.3	
24	0.5 mL Allyl methyl sulfone	1585.3	916.0	86	5.8	
25	0.5 mL Allyl methyl sulfone	1581.6	960.7	89	6.5	
26	**1 mL water standard 102 ppm**	**101.8**	**123.3**	**67**	**6.7**	**100**
27	1 mL 1 wt% Lithium acetate in AN	103.6	68.8	66	5.8	
28	1 mL 1 wt% Lithium acetate in AN	101.3	80.4	67	5.6	
29	1 mL 1 wt% Lithium acetate in AN	104.8	80.9	72	4.0	
30	1 mL 1 wt% Lithium acetate in AN	100.4	78.1	68	5.4	
31	1 mL 1 wt% Lithium acetate in AN	101.2	75.9	72	5.1	
32	**1 mL water standard 102 ppm**	**103.3**	**127.3**	**78**	**4.8**	**101**

CONCLUSION

The new Hydranal NEXTGEN Coulomat A-FA and C-FA reagents allow the accurate measurement of water content in

- many different types of electrolytes,
- as well as in their raw materials,
- including problematic additives such as VC, FEC and borates like LiBOB
- and ketones such as acetone



Added value:

- ✓ Reduced frequency of reagent change
- ✓ Faster titration – more analysis per day
- ✓ No need of additional documentation (CMR free, chloroform free)
- ✓ Universal reagents – one solution for all types of challenging samples

FA AVAILABILITY & PRICING

Product Number	Product Name	Description	Packaging	Pricing	Competitive Products
34471	HYDRANAL NEXTGEN Coulomat A-FA (anolyte)	Anolyte for coulometric Karl Fischer titration of ketones and Li-ion battery electrolytes, preferred for cells with diaphragm, acetonitrile-based, free of alcohols (free of CMR substances)	500 ml	+23% over Coulomat AK	**No competitive products!**
34470	HYDRANAL NEXTGEN Coulomat C-FA (catholyte)	Catholyte for coulometric Karl Fischer titration of ketones and Li-ion battery electrolytes, acetonitrile-based, free of alcohols (free of CMR substances)	10 × 5 ml ampoules	+29% over Coulomat CG-K	

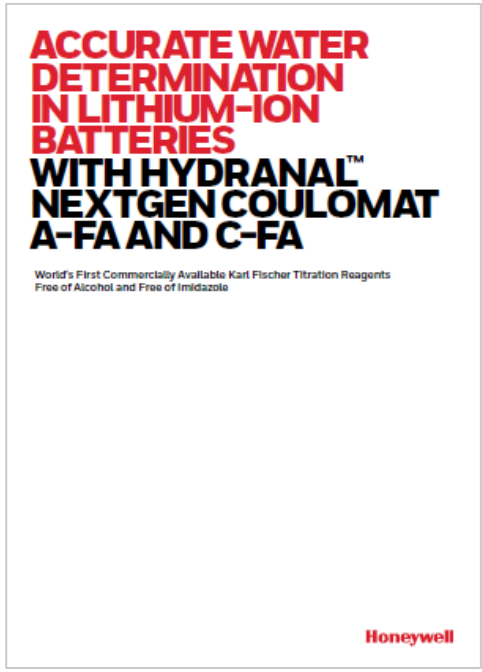
Added value:

- ✓ Reduced frequency of reagent change
- ✓ Faster titration – more analysis per day
- ✓ No need of additional documentation (CMR free, chloroform free)
- ✓ Universal reagents – one solution for all types of challenging samples

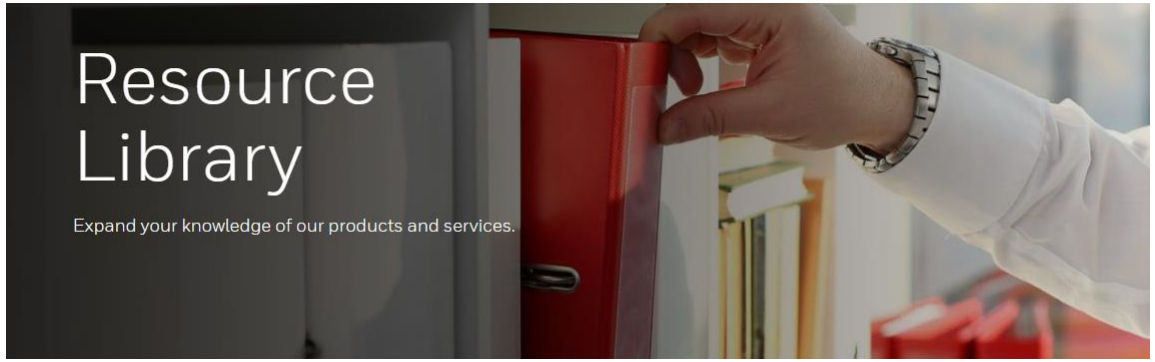
Stocking in Rhenus and Shanghai – other locations after confirming demand

FA MARKETING & TRAINING MATERIALS

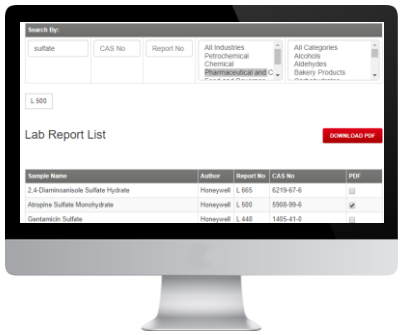
- Websites: for LiB and for other applications (coming soon)
- Technical information sheet T007 – recommended handling of water standards
- Technical information sheet T013 – how to use FA reagents correctly
- Product flyers: for LiB and for ketone applications
- White papers: for LiB and for ketone applications
- Official statement – no change in titration method needed



→ https://lab.honeywell.com/en/resources/resource-library

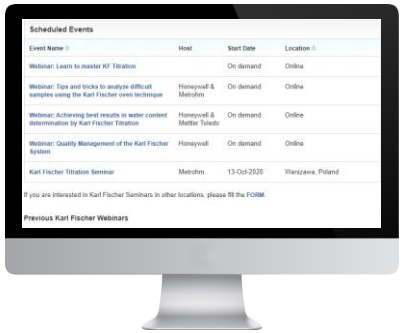


HYDRANAL ONLINE TOOLS



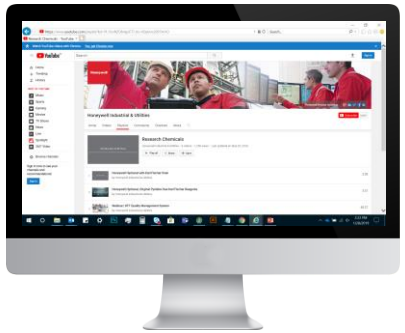
Hydranal Lab Reports database (Resources):

- **> 800 Lab Reports (includes Metrohm Application Notes)**
- **> 60 Ph. Eur. Suitability Tests Reports**



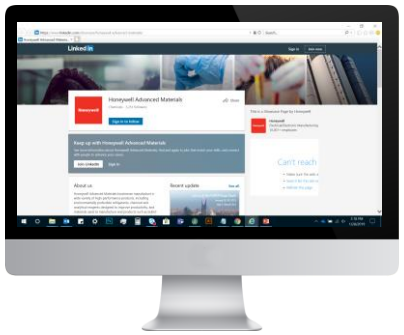
Honeywell Research Chemicals News & Events page:

- **incoming seminars**
- **incoming webinars**



YouTube Honeywell Research Chemicals playlist:

- **recorded webinars**
- **“How to” videos**



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- **invitations to events**

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THANK YOU

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