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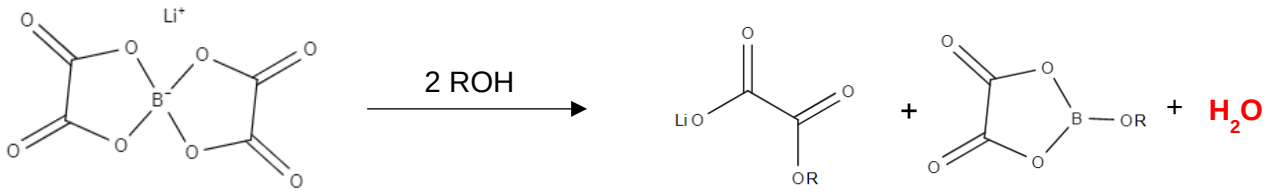
HYDRANAL™ Laboratory Report L 768

Karl Fischer (KF) Water Determination in Lithium Borates

Background: Lithium borates like LiBOB and LiDFOB are often used as additives in lithium-ion battery electrolytes (LIBs). Unfortunately, they react with alcohols, whereby water is released as a byproduct.



LiBOB

As a result, titrations in alcoholic KF reagents provide wrong results, which are highly overdetermined.

Examples:

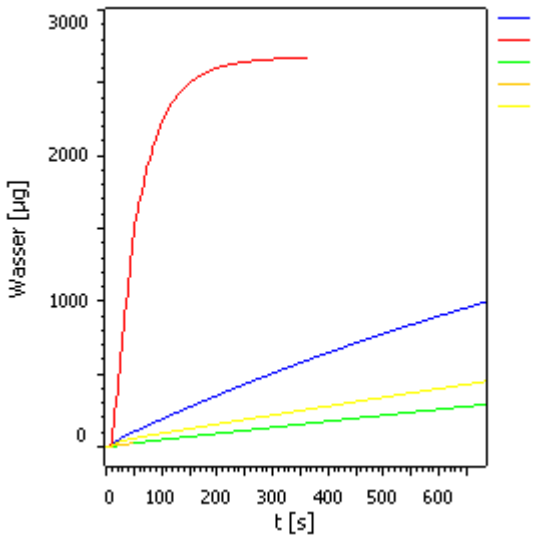


Fig. 1. Titration of 1 mL 5% LiBOB + 95% acetonitrile in different KF reagents

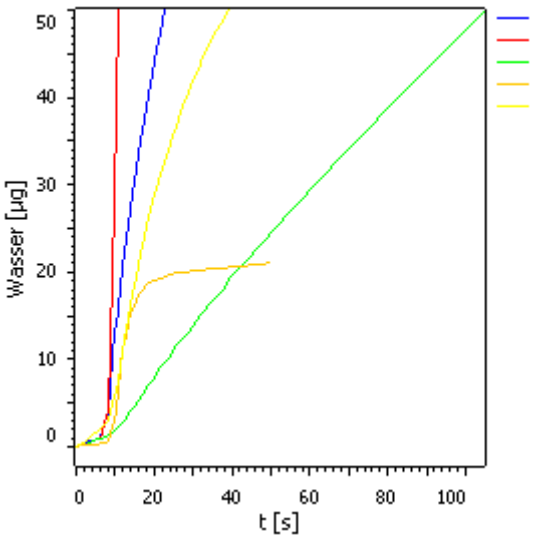


Fig. 2. Zoomed frame of Fig. 1.

Table 1. Titration of 1 mL 5% LiBOB + 95% acetonitrile in different KF reagents.

Color	Reagent	Water [ppm]	Deviation [%]	Comment
orange	HYDRANAL Coulomat A-FA[1] + Coulomat C-FA[1]	23.7	0	No side reaction; stable EP
green	HYDRANAL Coulomat AK[2] + Coulomat CG-K[2]	-	no EP	Ongoing side reaction
yellow	Reagent MK[2] (Anolyte + Catholyte)	-	no EP	Ongoing side reaction
red	HYDRANAL Coulomat AG[3] + Coulomat CG[3]	3224.8	13507	Side reaction completes fast
blue	Reagent M[3] (Anolyte = Catholyte)	-	no EP	Ongoing side reaction

LiBOB: lithium bis(oxalate)borate; LiDFOB: lithium difluoro(oxalato)borate
1: alcohol-free; 2: methanol-free; 3: methanolic

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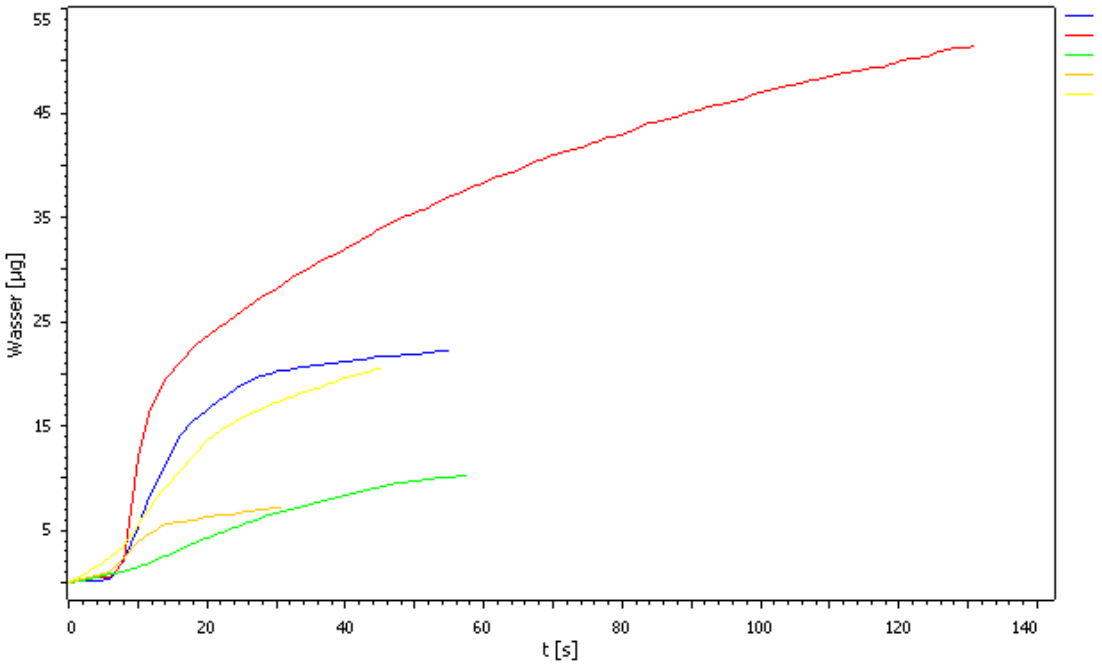

Fig. 3. Titration of 1 mL 5% LiDFOB + 95% acetonitrile in different KF reagents

Table 2. Titration of 1 mL 5% LiDFOB + 95% acetonitrile in different KF reagents

Color	Reagent	Water [ppm]	Deviation [%]	Comment
orange	HYDRANAL Coulomat A-FA[1] + Coulomat C-FA[1]	6.1	0	No side reaction; stable EP
green	HYDRANAL Coulomat AK[2] + Coulomat CG-K[2]	10.2	67	Side reaction with stable EP
yellow	Reagent MK[2] (Anolyte + Catholyte)	15.9	161	Side reaction with stable EP
red	HYDRANAL Coulomat AG[3] + Coulomat CG[3]	53.4	775	Side reaction with stable EP
blue	Reagent M[3] (Anolyte = Catholyte)	24.8	307	Side reaction with stable EP

Conclusion:

The side reaction of alcohols with LiBOB is very intensive. Only alcohol-free reagents like Hydranal Coulomat A-FA/C-FA provide correct results.
Methanol-free reagents like Hydranal Coulomat AK/CG-K and Reagent MK which utilize alcohol derivatives are not able to suppress water releasing side reactions.
With methanolic Hydranal Coulomat AG/CG stable endpoints are obtained, however the results are wrong, since they represent the amount of water from the sample plus water from the side reaction.

In samples that contain LiDFOB water releasing side reactions are less pronounced compared to LiBOB samples. However, they cannot be omitted completely by using methanol-free reagents.

Highly accurate water determination in borate containing samples is ONLY possible if alcohol-free KF reagents are used.

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Recommended reagents:

34471 HYDRANAL-NEXTGEN Coulomat A-FA (anolyte)
34470 HYDRANAL-NEXTGEN Coulomat C-FA (catholyte)

Recommended auxiliaries:

34446 HYDRANAL-Water Standard 0.1 PC
34241 HYDRANAL-Molecular Sieve 0.3 nm

Articles and Whitepapers:

https://lab.honeywell.com/en/hydranal/nextgen/alcohols-free-for-lib

Hydranal-Technical Information Sheets:

Hydranal Center of Excellence
Honeywell Research Chemicals

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