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HYDRANAL™ Technical Information Sheet T011

Color Change of Coulometric KFT Reagents

In coulometric Karl Fischer titration, iodine needed for KF reaction is not dosed directly from the titrating agent (like in volumetric method) but is electrochemically generated in-situ by oxidation of iodide present in coulometric anolyte. Iodine thus generated reacts with water from the sample and the titration end point is indicated by a small excess of iodine at the indicator electrode. If the method parameters are not set properly or the indicator electrode is covered with some impurities, the end point may not be detected correctly leading to excess iodine generation and over-titration. The presence of iodine or iodide is what results in the color of the solution. At equilibrium, the color of the solution is pale yellow. With the first excess of iodine the yellow become more intense and with clear excess of iodine the solution appears light to dark brown.

A similar oxidation processes can take place within the closed bottle of the anolyte e.g. when the bottle is stored in contact with UV light. Over time, small amounts of iodine can be generated by auto oxidation and result in reagent color varying from yellow to brown. This is more likely visible in pre-mixed reagents such as Hydranal-Coulomat AK, Hydranal-Coulomat Oil, or Hydranal-Coulomat AG-H, but can take place in all coulometric anolytes.

During production a small amount of water (in ppm range per specification) is added to the reagents to combat the effects of such oxidation and so originally, the reagents are colorless or pale yellow. This trace amount of water is normally eliminated by first pre-titration of reagent in coulometric cell. If any oxidation processes do take place in the bottle, the water present in the reagent reduces the iodine generated over time to maintain the original color of the reagent. Usually such auto oxidation processes are very weak, however under some storage conditions or over the long term can be strong enough to use all water present in the reagent resulting in an excess of iodine. As mentioned above, the more the excess of iodine produced, the darker color of the reagent. If the titration cell is filled with such a darkened reagent as is, the titrator indicates an end point parameter and is not able to start the conditioning mode. An error message such as “over-titration” will be shown.

Excess of iodine does not however influence the product quality or render a reagent completely unusable. The excess iodine simply needs to be reduced before the reagent can be used and this can be achieved in a few different ways. In most cases, it is enough to expose the reagent to humid air by carefully shaking the open bottle, preferably in a circular motion to maximize the exposure to humidity. The darkened reagent can be also poured back and forth from the bottle into a clean beaker to expose it to humid air repeatedly. If these methods are not able to reduce all the excess iodine formed or if the bottle is connected to the titrator via a tightly closed dosing system which does not allow for the methods described above, then a few drops of humid solvent can be added to the reagent instead, either to the whole bottle or to the aliquot in the titration vessel. Please note, only solvents already present in the original reagent formulation should be used. For example:

- for Hydranal-Coulomat AK use pure chloroform (do not use methanol as this is methanol free reagent),
- for Hydranal-Coulomat Oil use pure chloroform or xylene or methanol,
- for Hydranal-Coulomat AG-H use pure pentanol or methanol.

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For composition of other coulometric reagents, please check the product label or Safety Data Sheet. Please do not add pure water as while it will reduce the iodine, any excess of water will decrease the water capacity of the reagent and extend the conditioning time.

As iodine formation is accelerated by UV light, under some laboratory conditions, this may also take place when the reagent is left in the titration cell and not used for some time. In such cases, we recommend the same process of adding a few drops of proper humid solvent. It is not recommended to stir the reagent in the open cell as water from humid air can stick to the upper part of the cell and constantly increase drift. To avoid excess iodine formation in advance, if it is known that the titration cell is exposed to UV light (is located close to a window or artificial daylight lighting) we recommend using a cell made from dark glass or to cover the cell with aluminium foil when not in use.

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