



## HYDRANAL<sup>®</sup>-The Coulometric Cell

There are two different types of coulometric cells: those with a diaphragm and those without one. The diaphragm separates the anode chamber, where oxidation of  $I^-$  to  $I_2$  occurs, from the cathode chamber, where reduction of protons to  $H_2$  occurs. The cell without a diaphragm also has an anode and cathode, but the compartments are not separated. Proper care and maintenance of the coulometric cells will help maximize the sensitivity and reliability of Karl Fischer titrations made with them.

[www.sigma-aldrich.com/hydranal](http://www.sigma-aldrich.com/hydranal)

### The Anode Chamber

The actual water determination takes place in the larger anode chamber (see Figure). This chamber is filled up to the meniscus layer of the catholyte with the anolyte solution that contains the necessary reagents for the Karl Fischer reaction. In cells without a diaphragm approximately 100 mL of anolyte are added.

The necessary amount of iodine ( $I_2$ ) required for the titration of the water is formed from iodide ( $I^-$ ) at the anode. The amount of water titrated is calculated from the quantity of current necessary to produce the iodine.

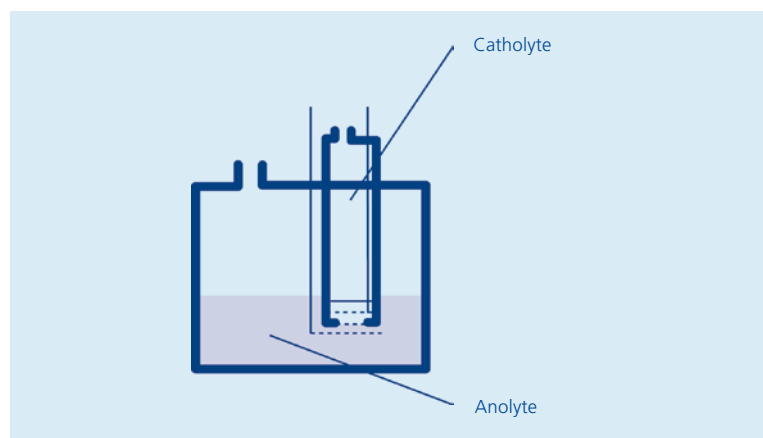


Figure ..... Coulometric Karl Fischer Titration

### Interferences in the Anode Chamber

If any iodine remains in the anolyte after it has been added to the anode chamber the machine will not start and an error message will be displayed. The injection of a small quantity of wet methanol or 2-methoxyethanol removes this excess iodine and the pre-titration will then start in the usual way.

Any moisture that seeps into the cell is removed automatically during the "conditioning phase". In spite of this, alcohol can condense on the upper walls of the cell and absorb moisture. This moisture, expressed as drift or background, has to be removed by occasionally emptying, cleaning and drying the cell.

### Sample pH and Conductivity

Reliable results from Karl Fischer titration require that the pH be maintained between 4 and 7. Samples capable of altering the pH value outside this range or that can react with iodine or alcohol may cause unwanted side-reactions and erroneous readings. Also, some samples can lower the conductivity of the reagents, which affects reliability of the measurement. In such cases an error message is given and the reagents have to be renewed.

### The Cathode Chamber

Typically 5 mL of catholyte are added to the cathode chamber. The cell is then set up in the same manner as the anode chamber. At the start of the coulometric Karl Fischer titration protons ( $H^+$ ) are reduced to hydrogen ( $H_2$ ). This is noticeable at the cathode where bubbles of hydrogen are clearly visible.

For cells with a diaphragm, its function is to prevent the iodine, which is generated at the anode, from being reduced immediately at the cathode causing erroneous readings. This problem is prevented in the cell without a diaphragm through modification of the cathodes construction.

### Interferences in the Cathode Chamber

In order to achieve accurate results the catholyte should be renewed at least weekly regardless of the quantity of water that has been analyzed in the cell.

Extraneous moisture must be kept from the cathode chamber. Water that accumulates there is never fully eliminated since the reaction that removes water takes place only in the anode chamber.

All catholytes, if they are used for too long, can produce an unpleasant odor, darken the electrode and form yellowish precipitates in the cathode chamber. If the catholyte has been in use for a long period of time other compounds dissolved in it will also be reduced. These drift through the diaphragm into the anodic chamber, cause high background and foul the diaphragm. The results obtained for the water content are then usually too high.

### Cleaning of the Coulometric Cell

In cells containing a diaphragm, reagents must be changed often enough to avoid build up of salts. This build up will cause a decrease in electron transfer across the diaphragm and lead to low recoveries and erroneous results. Since any solid can also block this diaphragm, solid samples cannot be analyzed with a coulometric system. Solids should be pre-dissolved and run against a blank.

The glass anode chamber itself is easy to clean using water or a suitable solvent. It can be dried in an oven at 50°C or under a gentle stream of warm air.

The generator electrode with a diaphragm can be cleaned by placing in a beaker of methanol. The methanol migrates through the diaphragm into the inner part of the chamber, thereby cleaning it. If there is visible contamination on any part of the cell, these procedures can be carried out with nitric or chromosulfuric acid and then repeated with methanol. Doing so will thoroughly clean the anode, diaphragm and cathode. In cells without a diaphragm, simply rinsing with water or a suitable solvent will clean the generator sufficiently. If there is blackening in certain areas, the anode or cathode chamber can be dipped in nitric or chromosulfuric acid and then rinsed with water or solvent. After the last rinsing process, the glassware can be dried as described for the cell with a diaphragm.

### Control of Accuracy

In order to control the accuracy of the reagent and the instrument according to ISO 9000 we recommend using HYDRANAL quality standards and reagents, including HYDRANAL-Water Standard 1.00 and HYDRANAL-Water Standard 0.10. A partial list of these standards appears in the Table; the full range can be found on our website:

[www.sigma-aldrich.com/hydranal](http://www.sigma-aldrich.com/hydranal)

### Product Information

The full range of product and instructional literature on our HYDRANAL products including our HYDRANAL-Manual, a handbook consisting of 120 pages on the Karl Fischer titration, and our new HYDRANAL-Multimedia Guide CD (Literature Code GVJ) is available by calling us or by visiting the HYDRANAL website:

[www.sigma-aldrich.com/hydranal](http://www.sigma-aldrich.com/hydranal)

### For technical help

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Table ..... Selected HYDRANAL Reagents and Standards

Cat No.	Reagents	Package Size
34807	HYDRANAL-Coulomat A	500 mL
34836	HYDRANAL-Coulomat AG	500 mL, 1 L
34810	HYDRANAL-Coulomat AD	500 mL
34726	HYDRANAL-Coulomat E	500 mL
34843	HYDRANAL-Coulomat AG-H	500 mL
34739	HYDRANAL-Coulomat AG-Oven	500 mL
34868	HYDRANAL-Coulomat Oil	100 mL, 500 mL
34829	HYDRANAL-Coulomat AF-7	1 L
34820	HYDRANAL-Coulomat AK	500 mL
34840	HYDRANAL-Coulomat CG	50 mL box with 10 x 5 mL ampoules
34821	HYDRANAL-Coulomat CG-K	50 mL box with 10 x 5 mL ampoules

Cat No.	Standards	Package Size
34828	HYDRANAL-Water Standard 1.00	40 mL
34847	HYDRANAL-Water Standard 0.10	40 mL
34748	HYDRANAL-Water Standard KF-Oven 220-230°C	10 g
34693	HYDRANAL-Water Standard KF-Oven 140-160°C	10 g

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