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The Photometry Dictionary

TIPS AND TRICKS FOR PHOTOMETRIC MEASUREMENTS –
FROM OUR CUSTOMERS' MAGAZINE
WATERWORLD

What does mercury-free COD measurement yield?

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What does mercury-free COD measurement yield?

In the frame of environmental protection, the efforts to minimize health-hazardous or environmentally relevant hazardous substances in all areas prevail. In this context, there is always the question whether the common COD cuvette quick tests that contain mercury, can be replaced with mercury-free test sets. But what does this mean for the quality of the measuring results?

The principle of COD measurement

COD is a sum parameter for many, very different substance combinations. The water sample with added sulphuric acid is heated with a defined volume of potassium chromate and the dichromate used up during oxidation is measured photometrically. This will yield the equivalent volume of oxygen. The solution also contains mercury sulphate to mask choride ions in the sample: The mercury sulphate then "catches" the chloride ions and becomes water-soluble mercury silver chloride that practically does not impact the measurement. Furthermore, silver sulphate is a catalyst for the oxidation reaction of the different complex organic substances.

The digestion effects, however, a much more complex due to possible side and cross reactions depending on the COD sample. This is the reason for the generally large tolerance ranges of COD tests compared to individual parameters.

Mercury-free COD tests

If you omit the mercury sulphate in COD test sets, chloride will create silver chloride as an oxidation substance from silver sulphate (in addition to many other possible effect, such as the creation of chlorine gas). The AgCl leads to clouding or hard to process precipitation. The complex reaction possibilities lead to non-reproducible measuring errors, with a significantly higher dispersion of the received measuring values.

The table shows comparative measurements between mercury and mercury-free COD measurements by means of a real sample in the inlet and discharge of a communal wastewater treatment site. The chloride content was at 140 mg/l in the inlet and 110 mg/l in the discharge and was increased step by step to examine the influence on the test series.

If chloride is present in mercury-free test sets, you will clearly notice the false high readings and the increased dispersion compared to ISO-compliant test sets. The effect of the step by step increase of the chloride content can be observed very well in the inlet. Therefore, these test sets are not suitable under normal usage conditions.

Environmentally friendly in spite of mercury: the common COD cuvette test

Today's cuvette tests offer ISO compliance while using the lowest possible volume of chemicals in a closed system, which practically prevents jeopardizing the user and an escape of the substances into the environment. Therefore, based on their high measuring accuracy, mercury COD tests today represent an outstanding solution for a sustained and optimized water monitoring. If the commonly used COD tests are disposed of and recycled properly, they do not pose a danger to humans and the environment.

Less reagents and higher precision

The more often you work in the optimal measuring range, the more precise the volume of environmentally relevant reagent use can be adjusted; and also, the more precise the measuring values will be because of decreased dispersion due to side reactions. Especially these possible side reactions show the requirement of a comparable uniform process for the digestion temperature and time as well as for the cooling phase outside the thermal reactor: With a so-called high temperature digestion with a quick cool-down, there may be results that deviate from the DIN procedure, e.g. by higher digestion and unsettled precipitation, which remains as clouding in the sample.

Conclusion

The mercury-free COD test sets prove to be less expressive under the commonly found conditions of communal wastewater and do not offer reliable results for monitoring.

OptRF

In June 2015 WTW introduced a completely new optical reagent-free COD measurement procedure (Opt RF) for discharge samples of municipal wastewater plants.

Inlet

Chloride content (mg/l)	COD mg/l (Inlet)		COD mg/l (Inlet, filtered)	
	COD Test C4/25	COD (Hg free) 09773	COD-Test C4/25	COD (Hg free) 09773
140	568	786	124	246
	570	710	124	240
400	408	612	109	270
	394	736	91	242
500	373	534	84	428
	338	640	93	354

Discharge

Chloride content (mg/l)	COD mg/l (Discharge)	
	COD-Test C3/25	COD (Hg free) 109772
110	20	30
	20	26
250	24	27
	21	28
350	17	24
	18	26