COD Analysis and REACH Authorisation

One of the most important methods for the analysis of waste water is the parameter COD. Since November 2002 we have had ISO 15705 available, this was the first international standard for the use of commercial available COD tubes. This standard was developed under the guideline of the British Standards Institution and got great support from several ISO member countries during the introduction phase

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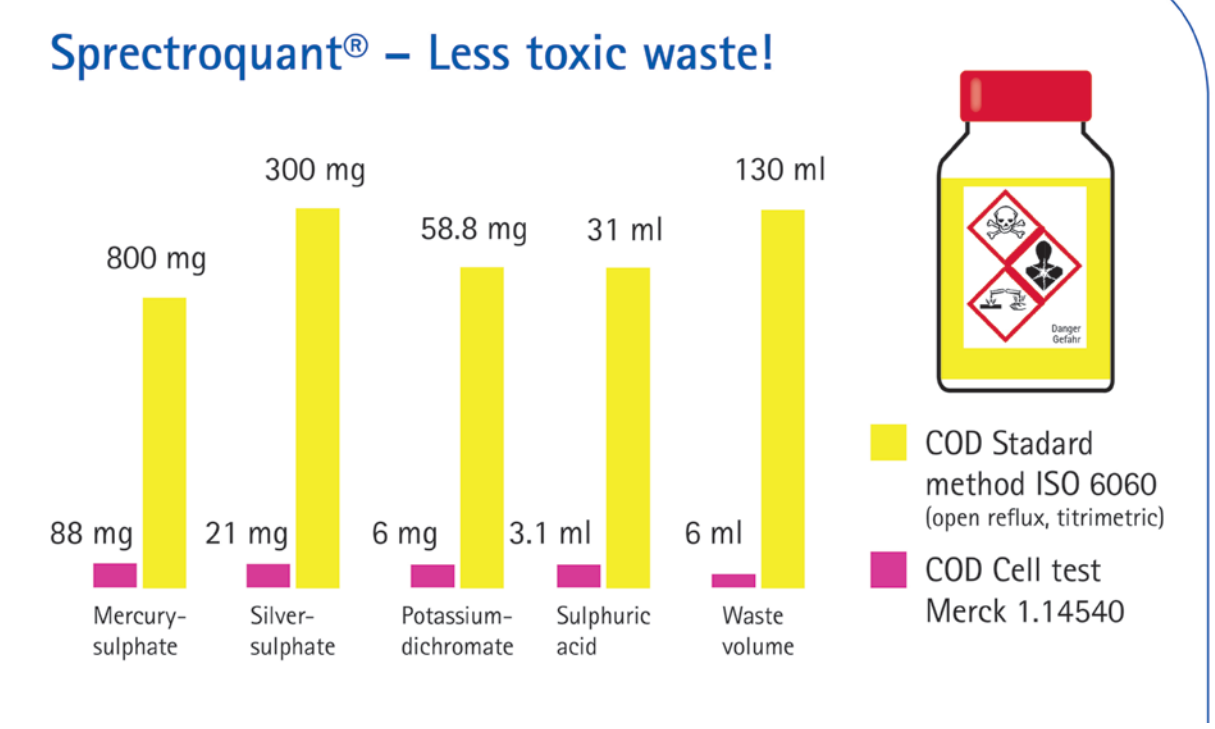


Picture 1: Used toxic substances for different COD methods

The implementation of this standard was a milestone and an important step for better protection of the environment. One of the very important reasons for establishing this standard was for easier and safer handling of the COD tubes in comparison to the open reflux and titration method and the reduction in the use of toxic reagents. Both standards, the ISO 6060 and the ISO 15705, work with potassium dichromate, silver sulfate, mercury sulfate, and sulfuric acid. There is a big difference between the quantities used per analysis from the classical method (open reflux and titration) in comparison to the COD tubes. Picture 1 shows an example of such a comparison of the required toxic substances for different COD tests.

The above picture shows that the commercially available COD Cell test uses around 90 % less toxic chemicals compared to the open reflux and titration method. The amount of toxic waste produced using the ISO 15705 is reduced by 90 % compared to the traditional ISO 6060 method with no loss in precision.

In the ISO 15705 there were 3 typical ranges specified (up to 50 mg/l, up to 150 mg/l, and up to 1,500 mg/l) whereas in the ISO 6060 only the measuring range from 30 – 700 mg is mentioned. In the EC Council Directive (91/271/EEC from May 21, 1991 concerning urban waste water treatment) a maximum limit for discharging COD into receiving water streams of 125 mg/l at a minimum percentage of reduction of 75 % is mentioned. This is the actual value for all EU Member States.

For the monitoring of this limit today commercially available COD tubes are almost always used. Not only waste water analysis is important. Many samples where COD analysis is done have different COD levels. Therefore, it is always better to choose the most appropriate range of the available test kit to get the most accurate results so as to avoid dilutions. That's why some suppliers have more COD tube ranges as mentioned in the ISO 15705. In picture 2 it shows which are the best kits to use depending on the average COD results obtained.

The two green ranges are new developments which have been requested by waste water users. The chloride tolerance depends on the measuring range but the minimum tolerance is 2,000 mg/l. Sometimes this will not be enough, then a dilution can be one option but there are also others.

Beside the above mentioned ranges Merck provides two more, very specialised COD tube ranges which can be used for samples with ultra-high chloride concentrations. Those samples are

for example seawater or waste water where chloride can be as high as 100,000 mg/l Cl or even more. Merck's latest development uses a depleting step with sulfuric acid to remove the chloride and a specially developed COD tube. This method allows the measurement of COD in the range of 5 – 60 mg/l and 50 – 3,000 mg/l in samples containing ultra-high levels of Chloride. This method is unique and allows the user to measure COD very accurately in e.g. seawater without dilution.

Replacement of COD

At the moment there are ongoing discussions at EU and national level to change from COD to another parameter (e.g. TOC or TOD) because of the toxic potential of potassium dichromate. Potassium dichromate is subject to authorisation under REACH. Authorisation intends to avoid the use of substances of very high concern wherever possible.

The determination of COD is a conventional method where the method defines the result. It can't simply be replaced by e.g. TOC method. There is no scientific alternative available for the measurement of COD that will give identical results. It is well understood that the results of TOC compared to COD will be different because all the circumstances are well defined and understood for the analysis of COD. Changing one parameter leads to different results.

COD tubes are generally:

- Easy to use
- The method is robust
- The results are accurate (see results of the round robin test which was done during the evaluation phase of ISO 15705.
- The tubes don't produce minimal exposure for the users because they are closed. COD Cell Tests reduce significantly the amount of hazardous substances used - like potassium dichromate.
- COD tubes are taken back and recycled by many suppliers.
- The use of commercially available COD tubes is cheap and safe.

The use of e.g. TOC will be more costly. Many users have to invest in expensive instruments. TOC results are expected to show greater variations between different labs compared to the ISO 15705 COD method. Therefore, we should have a look in the actual situation for the authorisation of potassium dichromate.

REACH Authorisation – Easing of tension for scientific R&D

The aim of the authorisation is to ensure that the risks of using substances of very high concern (SVHC) are properly controlled and that these SVHCs are progressively replaced wherever it is economically and technically viable. All uses of such a substance are forbidden after the sunset date unless an authorization is granted or the use is exempted from authorisation. One of these exemptions from authorization was granted for scientific research and development (SRD). A narrow interpretation by the authorities led - despite the SRD exemption - to the demand of an authorisation due to necessary upstream activities like filling, re-filling or formulation of a reagent. Practically, no exemption from authorisation for SRD would have existed and the sales of these reagents were threatened.

Legal Overview

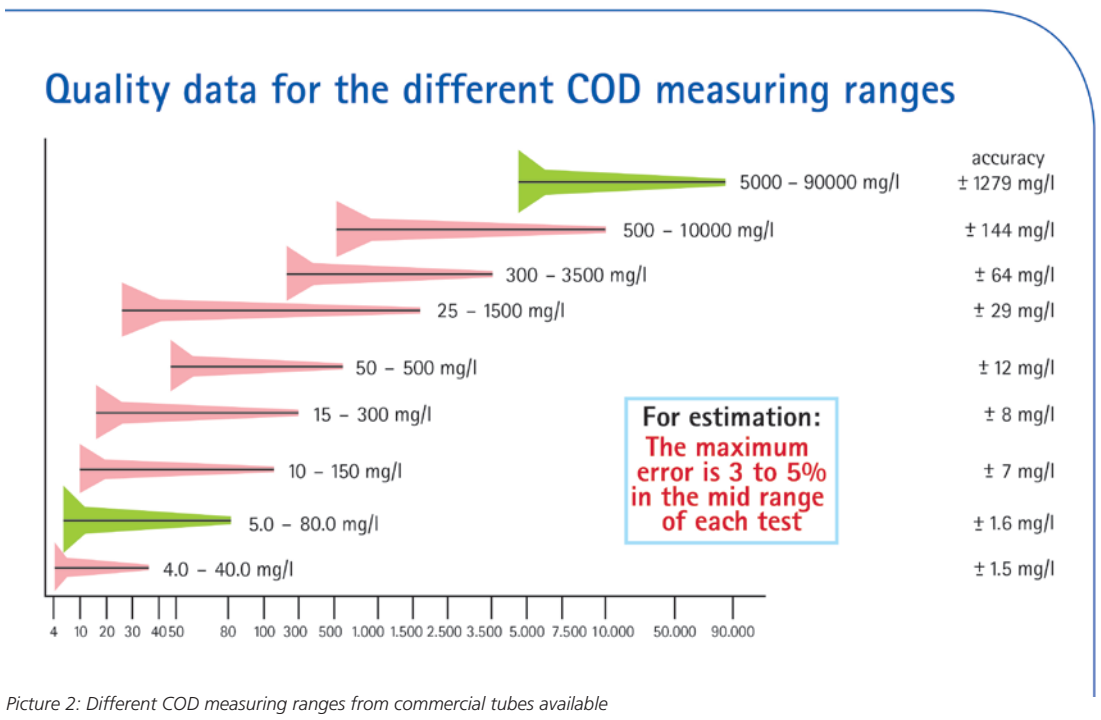
It is a multiple step process until a substance becomes a SVHC and is developed into Annex XIV of the REACH Regulation.

At first a Member State or the European Chemicals Agency (ECHA) indicates in the registry of intentions that a substance is in focus and information is collected. Sometime later the collected information is published and all stakeholders (e.g., industry, NGOs, authorities, individuals) can comment (public consultation). Finally, a decision is made whether the substance is included in the candidate list (currently 155 entries). If it is included, it becomes a substance of very high concern (SVHC). All remaining SVHCs on the candidate list are prioritized (once a year) whether they should be developed for Annex XIV. Usually a group of about 10 SVHCs is proposed for inclusion into Annex XIV combined with a second public consultation. The European Commission decides on inclusion into Annex XIV (currently 31 entries). The entry in Annex XIV triggers the authorization requirement. With the entry into Annex XIV a sunset date is fixed after which the substance can only be used for uses within a granted authorisation or for uses which are exempted from authorisation.

One of these exemptions was made for SRD. In the REACH Regulation SRD is defined in Art. 3 as follows:

"Means any scientific experimentation, analysis or chemical research carried out under controlled conditions in a volume less than one tone per year;"

The question whether routine analytical methods are covered by SRD was already answered in FAQ 585 by ECHA:



Picture 2: Different COD measuring ranges from commercial tubes available

[585] Does the exemption for the use of Annex XIV substances in scientific research and development under Article 56(3) REACH also apply to analytical activities such as monitoring and quality control?

REACH
Authorisation
Version: 1.0
Latest update: 21/01/2014

Yes, it does. Under Article 3(23) REACH, scientific research and development means any scientific experimentation, analysis or chemical research carried out under controlled conditions in a volume less than one tonne per year. Thus, scientific research and development can cover analysis, and a substance may be exempted from authorisation under Article 56(3) REACH if used, on its own or in a mixture, in analytical activities such as monitoring and quality control. For instance, routine quality control or release tests in laboratory scale using the substance as extraction solvent or analytical standard fall into the definition of 'scientific research and development' under Article 3(23) REACH and in the scope of the exemption foreseen in Article 56(3) REACH, as long as the quality control or release tests are carried out under controlled conditions and in a volume not exceeding one tonne per year and per legal entity.

Authorisation is a costly and time consuming process. ECHA recommends starting 18 months before the application date with the filing of the dossier. Alone ECHA's fees for checking the dossier are 53 000 EUR for a large company. This includes one use, one substance and one applicant. The application has to be renewed after the review period (4 - 12 years) causing the same costs for fees. Costs for the filing of the dossier are significantly higher.

Latest Development

End of November new entries in the Authorization FAQ were published by ECHA. Relevant for SRD and authorization is entry 1030:

[1030] Article 56 (3) of REACH exempts from the authorisation requirement the use of a substance in scientific research and development (SRD). Does this exemption also cover the life-cycle steps (such as formulation) preceding the end-use in SRD?

REACH
Authorisation
Version: 1.0
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Yes, the uses of a substance upstream preceding an exempted end-use in SRD are also exempted in quantities of the substance ending up in the SRD use (under 1 t/y) subject to what is set out below.

The definition of SRD in Article 3(23) requires any scientific experimentation, analysis or chemical research to be carried out "under controlled conditions" and "in a volume less than one tonne per year". Accordingly, the exemption in Article 56 (3) is delimited by a certain level of control of risks – i.e., use under controlled conditions and in a volume less than 1 tonne per year – which also apply to the upstream life-cycle stages preceding the end-use in SRD.

As shown above, the authorities moved away from the narrow interpretation of the SRD exemption. This has a major positive impact on the reagent business. All reagents for SRD containing an SVHC can continue to be produced and sold within Europe as long as the quantity of the SVHC does not exceed 1 t/a per legal entity. Necessary upstream activities in the production of a reagent for SRD are now covered by the SRD exemption. Product cancellations due to filling or formulation steps of reagents for SRD are no longer required.

But we should still think about substitution of SVHC during product development wherever it is possible.

During development of new reagents it should be examined whether the SVHC can be replaced.

If you have any questions, please do not hesitate to contact us at reach@merckgroup.com.

Additional information on authorisation as well as other REACH-related topics can be found on the website (http://echa.europa.eu/) of the European Chemicals Agency (ECHA) in Helsinki, Finland.