

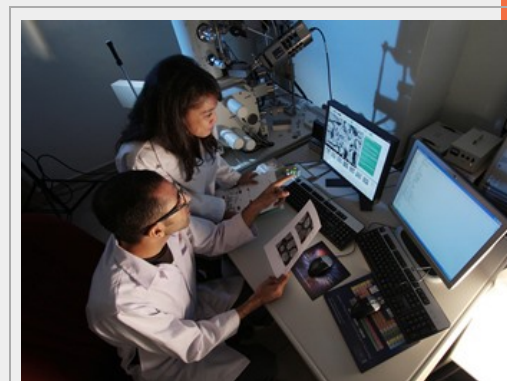
# COD (CHEMICAL OXYGEN DEMAND) ON-LINE MEASUREMENT DEVICE

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## ABSTRACT

COD (Chemical Oxygen Demand) is a widely known parameter used to measure water quality. It is a measure of water pollution resulting from organic matter. This parameter is defined as the amount of oxygen required, or equivalent, for the oxidation of all chemically oxidizable matter contained in a water sample.



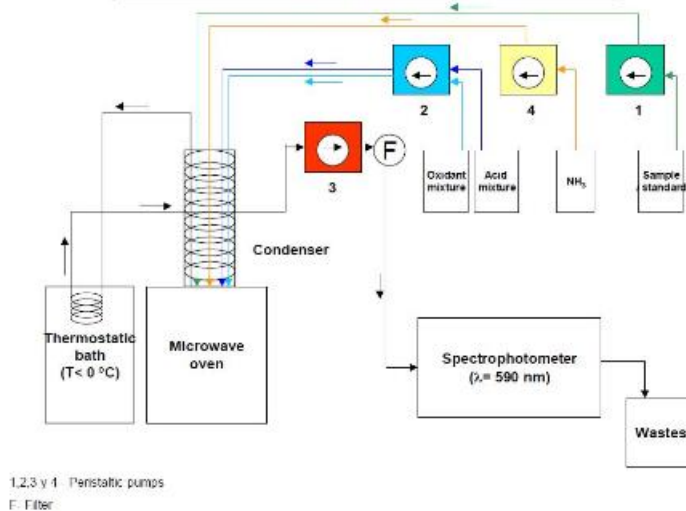
## TECHNICAL DESCRIPTION

The common method employed to obtain COD value is known as the Standard Method. In this method a known excess of potassium dichromate is used as the oxidizing agent and the sample is heated with a Hach digester for approximately two hours. The main problem of this method is the low efficiency of the heating method used to heat the reaction mixture and, hence, the time of reaction is too long.

The COD automatic measurement device, developed by the Department of Analytical Chemistry of the University of Alicante, can obtain the value of this parameter just in 10 minutes. This significant reduction in the reaction time is due to the fact that microwave radiation is used as the heating method.

The device is fully automated and controlled by PC. A specific software has been developed for this application. The software is user-friendly and allows the modification of all parameters individually.

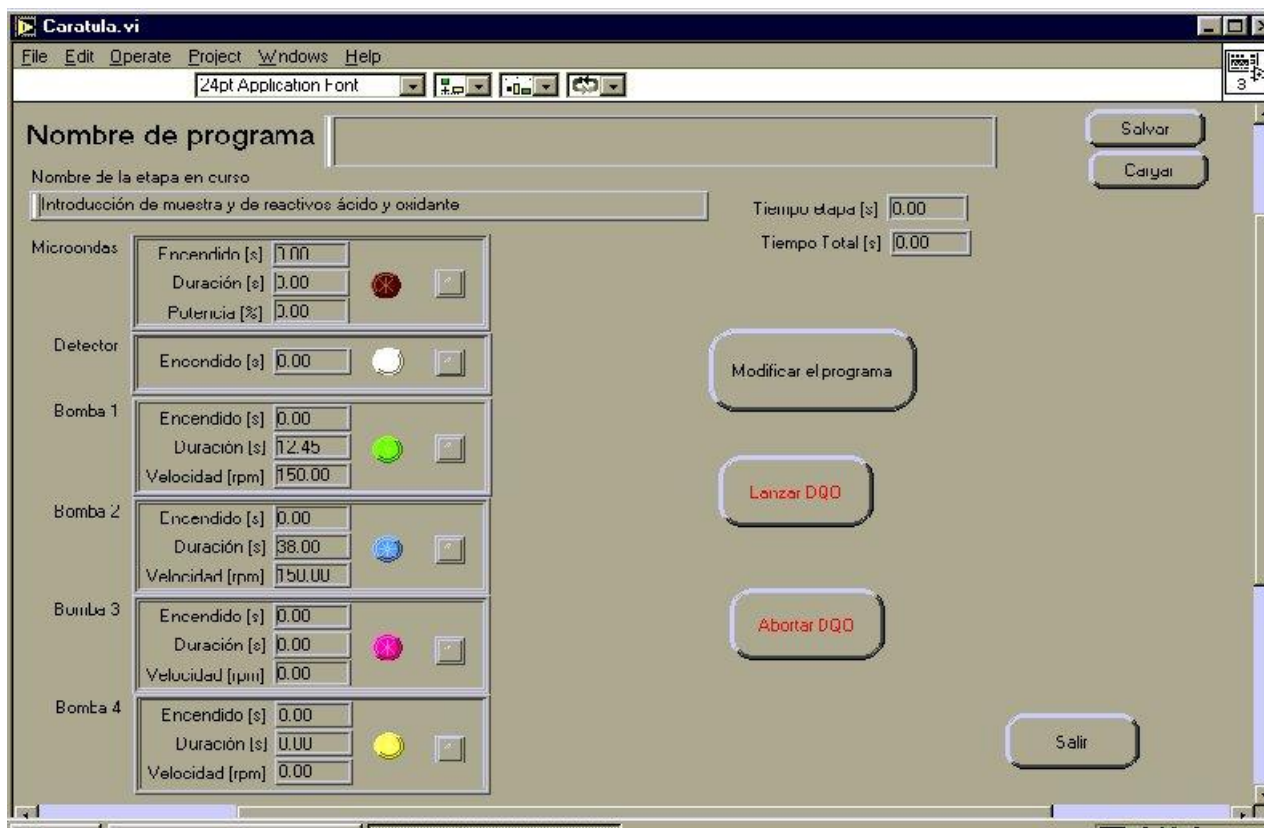
### SCHEME OF COD AUTOMATIC MEASUREMENT DEVICE



Sample goes into the measurement device through the pump number 1, which leads the sample into the microwave oven. Simultaneously, acid and oxidant mixtures are added into the microwave oven through the pump number 2. After adding the sample and reagents, the program starts automatically the reaction mixture irradiation with microwaves. Microwave radiation catalyses oxidation of organic matter by potassium dichromate, so oxidation is completed just in 8 minutes. Then the reaction products go into the spectrophotometer by the pump number 3, where the absorbance of Cr(III) generated during the sample oxidation is measured at 590 nm. This value is directly related with the amount of organic matter oxidised. Then, the software calculates the sample COD value, from the corresponding calibration curve. After measuring, waste produced goes into a container. Finally, the system is cleaned with concentrated ammonia added by the pump number 4.

The specific software designed to control automatically this device contains several subroutines for each step: sample COD measurement; system calibration with standards, etc. Each subroutine is also divided in different stages of: sample and reagents loading; heating; measuring; cleaning, etc.

Every parameter involved in each of these stages can be modified. These possibilities facilitates to adapt the program to the specific characteristics of different water samples. This is a notorious advantage, as it allows to measure the COD value of different samples (fresh water, waste water, etc) just by modifying the programme parameters.



### TECHNICAL SPECIFICATIONS

Measuring time: between 12 and 15 minutes, depending on each sample.

Sample maximum concentration: 15.000 mg O<sub>2</sub>/L.

System Calibration Frequency: daily

### COMPARISON BETWEEN THE CONVENTIONAL METHOD AND THE COD MEASUREMENT DEVICE

	Conventional method	COD automatic measurement device
<b>Time of reaction</b>	2 hours	12 – 15 minutes
<b>Heating method</b>	Conductive-convective, using a Hach digester	Microwaves
<b>Reagents used</b>	<ul style="list-style-type: none"> <li>• <b>OXIDANT MIXTURE:</b> [K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>]=0.0167–0.0670 M [H<sub>2</sub>SO<sub>4</sub>]= 3 M [HgSO<sub>4</sub>]= 0.11 M</li> <li>• <b>ACID MIXTURE:</b> [H<sub>2</sub>SO<sub>4</sub>]= 97% (m/m) [Ag<sub>2</sub>SO<sub>4</sub>]= 10 g/L</li> </ul>	<ul style="list-style-type: none"> <li>• <b>OXIDANT MIXTURE:</b> [K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>]= 0.12 M [H<sub>2</sub>SO<sub>4</sub>]= 2 M</li> <li>• <b>ACID MIXTURE:</b> [H<sub>2</sub>SO<sub>4</sub>]= 70% (m/m) [Ag<sub>2</sub>SO<sub>4</sub>]= 7 g/L</li> </ul>
<b>Quantitation method</b>	Titration the excess of dichromate with Mohr salt	Spectrophotometric measurement of Cr(III) absorbance
<b>Chloride interference</b>	Important	Absent up to 8.000 ppm

The main innovative aspects of this new device are:

- Significant reduction in the reaction time, in contrast with the conventional method.
  - Fully automated, flexible and easy-to-handle equipment.
  - Absence of chloride ions interference up to a concentration of 8.000 ppm
  - Useful for all kinds of water samples, including hardly oxidizing samples such as phenolic samples. It can measure up to 3.000 ppm of phenols.
  - No previous system for sample treating or conditioning is required.
- Produces a small amount of waste and the use of Hg salts is not required due to the absence of chloride ions interference.

### CURRENT STATE OF DEVELOPMENT

A laboratory prototype is currently available for testing. This device is being applied nowadays to an industrial site in order to measure waste water with high level of chloride.



#### MARKET APPLICATIONS

COD automatic measurement device can be used for the analysis of any waste water stream, both in continuous or in batch. Due to its high level of flexibility, automatization and simplicity of handling this device can be used in at-line, online and in-line modes. It can be applied to waste water treatment and purification plants, urban as well as industrial, and to the control of processes that made use of waste waters in which the quality of water is critical.

#### COLLABORATION SOUGHT

Two types of cooperation are sought by the Department of Analytical Chemistry of the University of Alicante:

- Transfer the design and manufacturing know-how of this device to companies involved in analysis equipment that may be interested in its marketing.
- Design and manufacture this device particularly for any company/institution interested in at-line, on-line and in-line measurements.

#### INTELLECTUAL PROPERTY RIGHTS

Dr. Antonio Canals, from the Department of Analytical Chemistry of the University of Alicante (Spain), owns the design and manufacturing know-how of this COD automatic measurement device.

#### RESEARCH GROUP PROFILE

One of the main scientific interests of the research team that has developed the device is to suggest new analytical methods or instrumentation prototypes both based on microwave radiation. In this sense, the team has published two articles on using microwave radiation as a way to reduce time of reaction in sewage COD measurement. The suggested device is based on both articles. Besides, one chapter on this issue has published in the book "Handbook of Water Analysis". All these works were done in collaboration with several University Departments and companies interested in sewage treatment.

#### MARKET APPLICATION (2)

Pollution and Environmental Impact

