

METHOD STATEMENT



Determinand:

Chemical Oxygen Demand (COD), (Total, Settled & Filtered)

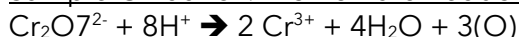
Matrix:

Sample Type: Final effluents, trade discharges, crude sewage and other related waste waters.

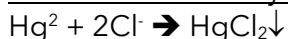
Principle of Method:

Samples are oxidised by heating in tubes containing sulphuric acid, potassium dichromate as an oxidising agent in the presence of silver sulphate as a catalyst. Mercuric sulphate is also present to suppress chloride interference. The dichromate is reduced to chromate during the digestion, for the LCK 1014 tubes the chromate produced is measured at 605nm but for the LCK 314 tubes the dichromate remaining is measured at 448nm.

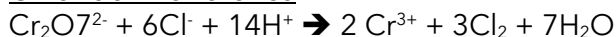
Sample Oxidation/Dichromate Reduction



Chloride removal by Mercuric Sulphate



Chloride Interference



Sampling and Sample Preparation:

Samples are normally taken in 1L PET bottles.

Samples should be analysed as soon after receipt as possible.

Samples are stable for 6 days from sampling (In-House Data - Coventry). If not immediately analysed samples should be refrigerated at $3\pm 2^\circ\text{C}$.

Interferences

If not suppressed chloride will cause positive interference. Inorganic reducing agents such as nitrites, sulphites and ferrous salts will contribute to the COD. Oxidising agents, e.g. Cr VI salts, can give false negative and low results. Bromide interference will not be controlled by mercuric sulphate.

Performance of Method:

Range of Application:

19 - 2000mg/l as O without dilution

LCK 314 15 - 150 mg/l as O

LCK 1014 100 - 2000 mg/l as O

Normal Reporting Level 19 mg/l as O

Limit of Detection:

18.83 mg/l as O (LCK1014)

6.26 mg/l as O (LCK314)

Recoveries of Compounds, Bias:

(LCK1014) Standards - Precision and bias

	Low Standard	High standard	1200mg/l AQC	Resorcinol
COD mg/l	400mg/l	1600mg/l	1200mg/l	125mg/l
RSD %	1.57	0.53	0.89	2.51
Bias %	0.39	-0.66	-0.30	-0.26

METHOD STATEMENT



Samples and Spiked Samples

	Final Effluent		Final Effluent Filtered		Trade Discharge		Crude Sewage		Raw Surface	
Spike Level	125	80%	125	80%	20%	80%	20%	80%	20%	80%
COD mg/l	126.4	1575.1	123.9	1556.5	373.2	1493.4	377.3	1465.2	410.0	1593.2
% Recovery	94.97	98.06	97.90	97.17	98.60	95.45	99.53	94.37	99.37	98.79
% RSD	3.35	1.75	4.20	1.50	2.41	0.87	4.12	1.77	2.17	0.72

LCK314) Standards - Precision and bias

Determinand	Low standard		High standard	
	Tot. RSD %	Bias %	Tot. RSD %	Bias %
COD	6.81	-2.26	2.82	0.54

Samples and Spiked Samples

	Final Effluent	River sample	Trade Discharge	125mg/l Resorcinol
Concentration mg/l as O mg/l	28.71	13.26	227.90	124.69
% Recovery	98.05	105.16	97.25	99.75
RSD	4.90	4.94	2.10	1.63

References:

Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1977. HMSO Methods for the Examination of Waters and Associated Materials. ISBN: 011 7512494.

Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1986 (Second Edition). HMSO Methods for the Examination of Waters and Associated Materials. Method B. ISBN: 011 7519154.

HACH Water Analysis Handbook 1997. Method 8000, Oxygen Demand, Chemical. ISBN: 23196-01.

COD analysis of saline waters - an investigation into chloride interference suppression. In-house investigation report. P Clark MDPC 046. 2002.