

Craig Goch Project – UWIST

Report No. 8

Methods of Chemical Analysis

Parameter	Method	Detection Limit*	Accuracy*
		(mg.1 ⁻¹ unless otherwise stated)	
Turbidity	ARPWW	0.2 Formazin Units	± 0.4 F.T.U.
Colour	ARPWW	5 Hazen Units	± Hazen units
Reactive silica	ARPWW	0.05	± 0.05
Chloride	ARPWW (Mercuric nitrate titn)	0.2	± 0.2
Sulphate	ARPWW (Turbidimetric	0.3	± 0.3
Orthophosphate	ARPWW	0.001	± 0.001
Total phosphorus	ARPWW	0.001	± 0.001
Alkalinity	Conductometric titn. (1)	0.2	± 1%
Ammonia	Modified Indophenol Method (2)	0.002	± 0.004
Nitrate	Cu/hydra zinc reduction, determined as nitrate	0.4	± 0.01
Nitrate	Griess-Ilavay reaction (3)	0.0003	± 0.0003
pH	pH meter, corrected to river temperature (4)	-	± 0.01 pH
Free CO ₂	Nomograph (4)	?	?
Soluble organic carbon	TOC analyser (5)	0.04	± 0.02
Particulate organic carbon	Dry, oxidation of particulate matter, analysis of CO ₂ by TOC analyzer (6)	?	?
Dissolved solids	250ml sample, filtered through CF/C filter, filtrate evaporated to dryness in weighed vessel, heated to constant weight at 180°C	0.4	± 0.8
Suspended solids	1 ltr. Sample filtered through weighed GF/C filter, dried at 105°C	0.1	± 0.2
Ash	Filter paper ignited at 500°C for 30 mins.	0.1	± 0.2
Chlorophyll	Sample filtered through CF/C filter, ? filter extracted with methanol, measured in 4cm cells at 665 & 750nm.	?	?
Humic acid	Precipitation method (7)	?	?
Conductivity	Conductivity meter	0.1 $\mu\text{s. cm}^{-1}$	± 1 $\mu\text{s. cm}^{-1}$
Temperature	Mercury-in-glass thermometer	-	± 0.5°C
Pesticide screen	GLC (8)	?	?
Fish tissue analysis	Atomic absorption (9)	-	-
Heavy metals: (soluble) (total)	Filtered <i>in situ</i> (GF/C), 5ml 1 : 1 HNO ₃ /1; as total metals		
	250ml evaporated, 5ml conc. HNO ₃ added, evaporated to dryness, taken up in 5ml 1 : 1 HNO ₃ , made up to 25ml.		
Total hardness	Calculations from concentrations of calcium and magnesium	-	-

Metals

Metal		Wavelength (nm)	Band-pass (nm)	D.L.	Accuracy
Ha	(Atomic emission)	589	2	0.1	± 0.1
K	(Atomic emission)	766.5	2	0.1	± 0.1
Ca	(Atomic emission)	422.7	2	0.1	± 0.1
Mg	(Atomic absorbsion)	285.2	2	0.1	± 0.1
Fe	(Atomic absorbsion)	248.3	0.2	0.1	± 0.1
Pb	(Atomic absorbsion)	283.3	0.7	0.001	± 0.003
Cu	(Atomic absorbsion)	324.7	0.7	0.001	± 0.003
Cd	(Atomic absorbsion)	258.8	0.7	0.001	± 0.003
Ni	(Atomic absorbsion)	232.0	0.2	0.05	± 0.05
Zn	(Atomic absorbsion)	213.8	2	0.01	± 0.01
Mn	(Atomic absorbsion)	280	0.7	0.001	± 0.003
Cr	(Atomic absorbsion)	357.9	0.2	0.01	± 0.02

Air/acetylene flame used.

Methods

ARPWW – Analysis of Raw, Potable, and Waste Waters (H.M.S.O.)

- 1) 100 ml sample titrated with N/10 HNO. Equivalence point found from graph of conductivity against volume of titrant as the interaction of two straight lines. There is good agreement between this method and potentiometric titration.
- 2) This is a manual adaptation of the Autoanalyser method. Ammonia reacts with phenol and sodium hypochlorite under alkaline conditions to form an indophenol type compound. Sodium nitroprusside acts as a catalyst. EDTA and sodium citrate are added to complex metal ions which might otherwise interfere. Colour measured in 4 cm cells at 635 mm.
- 3) Two methods have been used:
 - a) Sulphanilamide was reacted with nitrate ion and the resulting diazonium compound coupled with N-1 naphthylethylenediamine dihydrochloride, the colour being read at 540nm in 4cm cells.
 - b) As the latter reagent is carcinogenic, the ARPWW method using sulphonilic acid and Cleve's acid has been used instead.
- 4) Dye, J.F., *J. Am. Wat. Wks. Assoc.* **44** 356-372 (1952).
- 5) Filtered sample made pH 2 with HNO₃, carbon dioxide removed by bubbling CO₂ free air into sample. Sample introduced into Oxidation furnace containing copper oxide at 950°C via peristaltic pump. Resultant CO₂ mixed with hydrogen and passed over a nickel catalyst at 425°C. CO₂ reduced to methane which is measured by a flame-ionization detector whose output is recorded by a potentiometric recorder. Standards prepared from potassium hydrogen phthalate.

- 6) Solid heated at $> 500^{\circ}\text{C}$ in a stream of oxygen to oxidise carbon to CO_2 which is mixed with hydrogen as above. (This is only a tentative procedure which is yet to be set up).
- 7) 250ml sample evaporated to dryness and taken up in 5ml water. Solution filtered on GD/C filter paper and washed. Filtrate treated with lead nitrate solution to precipitate lead chromate. After 2 hours precipitate filtered on weighed CF/C filter paper, washed, dried at 105°C and weighed.

Lead content of precipitate found by destroying precipitate with potassium persulphate and titration of liberated lead ions by $\text{K}_2\text{Cr}_2\text{O}_7/\text{TA}$. Weight of humic acid found by difference. (This procedure has not been fully worked up as yet).

- 8) 500 ml samples will be collected in stoppered glass bottles and extracted by organic solvents. After separation by GLC using suitable columns organo-chlorine compounds will be detected by electron-capture detector and organo-phosphorus compounds by flame-ionisation detector. Detection limits and accuracies depend on compounds.
- 9) Dried and weighed fish tissue (individual organs of white fish, whichever is more convenient) will be heated in a muffle furnace to destroy organic matter. The residue will be extracted with as small a volume of 1 : 1 nitric acid as possible and made up to a convenient volume with distilled water. Heavy metals will then be determined by atomic absorption spectrometry.

Sample Preservation

Samples are collected in 2½ litre screw top, wide mouth, hard plastic bottles. At the time of collection small sub-samples are taken for phosphorus and nitrogen analyses. Phosphorus samples are held in 60ml hard plastic screw top bottles and 0.6ml 8N sulphuric acid is added as preservative. Nitrogen samples are held in 150 ml glass screw top bottles. Nitrogen and phosphorus samples are analysed as soon as possible.

On return to the laboratory 1 litre of sample is filtered through GF/C filter paper and the filtrate stored at 4°C in iodised plastic bottles for analysis of other parameters.

Samples for total metal analysis are preserved in plastic bottles with the addition of 5ml 1 : 1 nitric acid per litre.

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*Detection limits and accuracy estimated from calibration graphs, etc. A statistical analysis of each method has not been performed as yet.