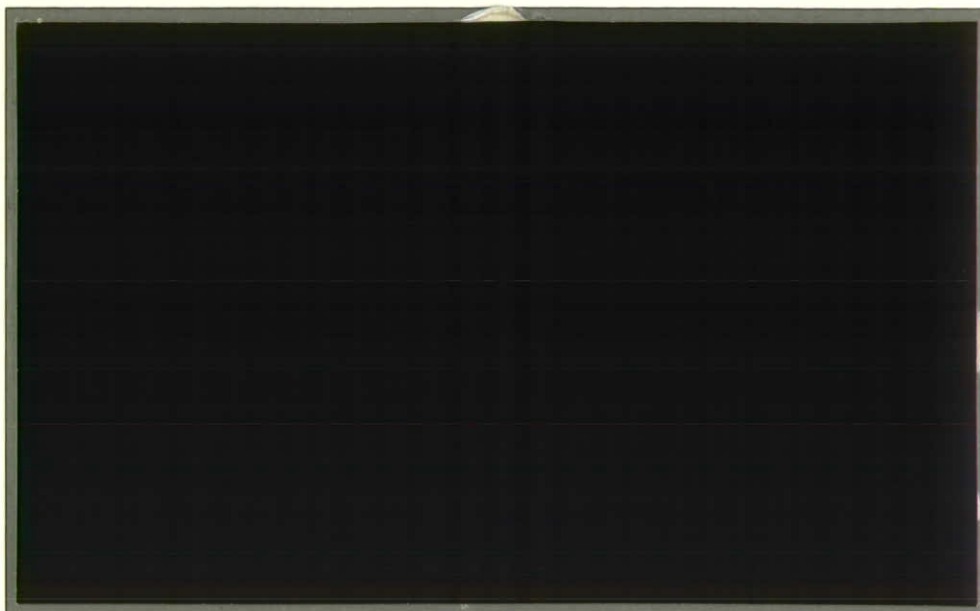


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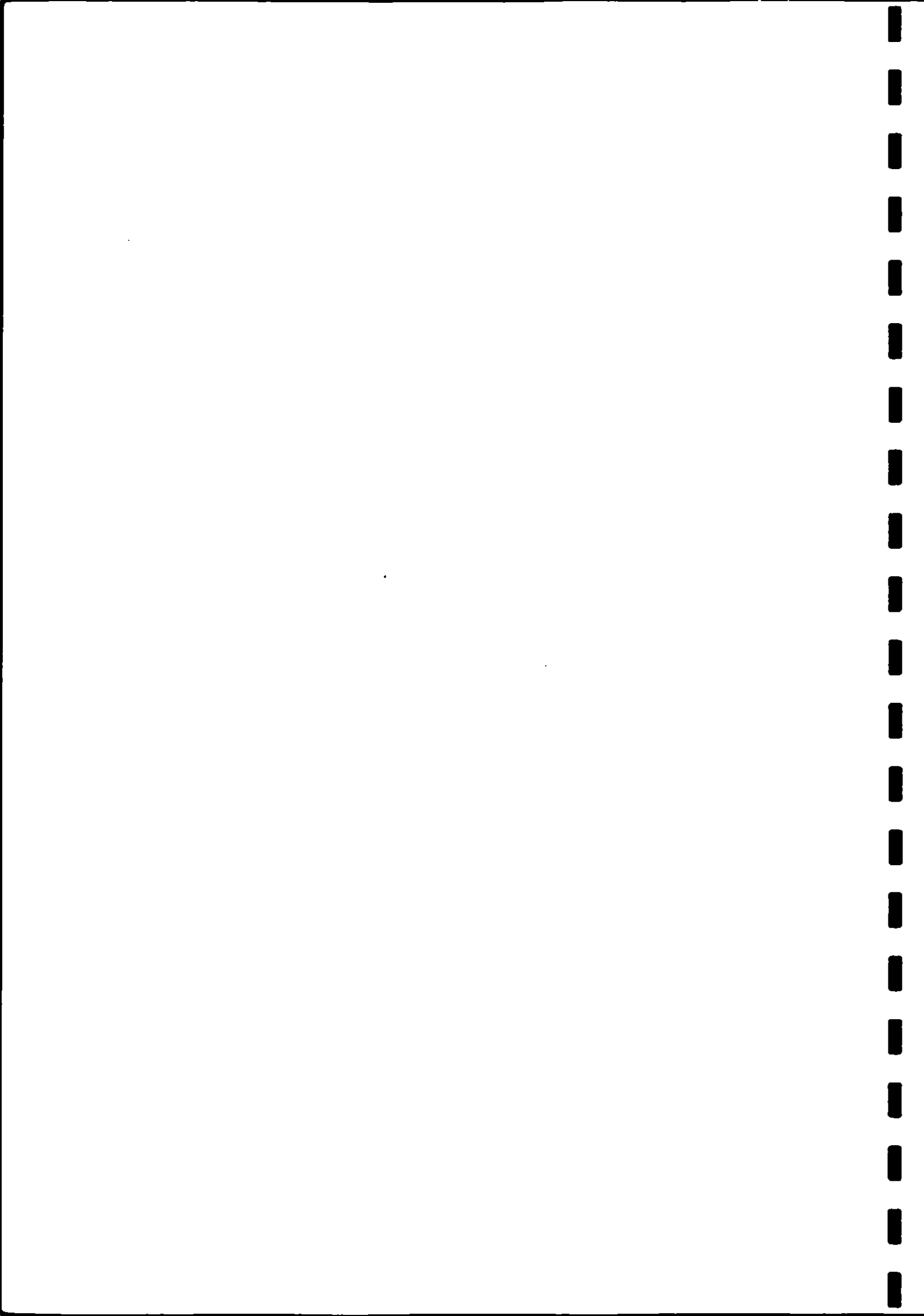
North Western Ethylene Pipeline Project
Recommendations for Monitoring of river
crossings sites during construction

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Summary

Recommendations are given for the type of and duration of monitoring, the crossing sites requiring continuous monitoring during construction, together with data on the relevant methodology and instrumentation for dissolved oxygen, suspended materials (or suspended solids) and discolouration. Hand-held instruments are recommended for use by environmental inspectors to test the water downstream of construction sites on their regular site visits, whereas a reduced set of the more sensitive sites require continuous monitoring during construction to provide data and to ensure adherence to contracts and to company environmental policy. Broadly, all of the larger wet crossing sites, except those with minimal established environmental value, are recommended for continuous monitoring together with representative dry crossing sites particularly those with high environmental value, unstable banks or beds, special features, and examples early in the work programme of each group of contractors to establish that good working practices are being applied. Recommendations for monitoring crossing sites for dissolved oxygen and/or suspended material have been graded and dependant upon the number of bore crossings, number approximately 8 essential, 28 highly advisable, a further 38 should be seriously considered and another 25 could be monitored; the remainder, c100, are not considered necessary to monitor. The sources of suspended material are discussed with suggestions for amelioration or prevention during construction particularly controlled rates of working for excavators, minimising bank removal and provision for desilting of rainwater etc. from the main trench.

Data is also included for a short training course on compliance with water pollution law, on sensors suitable for spot sampling together with their calibration procedures, and on the operation and range of equipment available for the prevention and clean-up of oil spills, etc.

Table of contents

	page
1 Introduction	3
2 Types, sites and methodology of monitoring the physical effects on water of construction activities	
2.1 Recommendations for types of monitoring	5
2.2 Recommendations for sites requiring monitoring	6
Table 2.2.1 Recommended monitoring sites	7
2.3 Recommendations for monitoring methodology and equipment	15
3 Sources, moderation and prevention of suspended material in watercourses	
3.1 Sources of suspended material	19
3.2 Recommendations for sediment control	19
4. Water pollution, prevention and clean-up	
4.1 Water pollution law	21
4.2 Behaviour of oil spills	23
4.3 Containment, removal and reclamation of oil spills	26
4.4 Prevention of pollution during re-fueling operations	32
5 Recommendations	33
6 References and Reports	34
 Appendices	
Appendix 1 List of suppliers and agents for monitoring equipment for dissolved oxygen, water temperature water turbidity and data loggers	37
Appendix 2 List of inland oil-spill recovery equipment manufacturers and suppliers	41
Appendix 3 Information for training course	44

1 INTRODUCTION

1.1 Background

Shell Chemicals UK Limited (SCUK) is to construct a pipeline system from the BP Grangemouth Refinery to Shell UK Stanlow Refinery. This new pipeline is to be known as the North Western Ethylene Pipeline (NWEPI). The object of this new pipeline system is to enable the transportation of ethylene in a dense phase directly from Grangemouth to Stanlow.

NWEPI consists of approximately 411 kilometres of '10 inch' (250 mm) diameter pipe with two pumping stations, twenty five block valves, pigging facilities, and two metering stations. Interconnection facilities at Grangemouth admit ethylene to the pipeline and into the existing high and low pressure pipelines at Stanlow. There are also SCADA and communication systems, cathodic protection systems, operation and maintenance facilities.

1.2 NWEPI Environmental Requirements

The project environmental policy (Environmental Statement, NWEPI, SCUK) recognizes that the successful execution of the project relies on the identification of potential environmental impacts and the definition and implementation of appropriate mitigation measures.

Previous environmental studies given in the Environmental Statement have been used to define the route by identifying constraints within progressively narrower corridors. Further studies to date have involved the collation of existing information or the use of remote sensing and the collection of on-site data including Dawson *et al* 1990, reports RL1-RL9, for aquatic sites. These latter surveys accurately located sites with environmental or conservation interest.

1.3 Objectives

The objectives of this report are to

1. recommend the type, site and methodology of monitoring with particular consideration to dissolved oxygen, suspended solids and discolouration for short-term (or spot-sampling) and for long-term monitoring ie. during the entire period that contractors are on-site, with recommendations and costs for suitable monitoring equipment which is easy to use and reliable;

2. discuss the mechanisms by which suspended solids arrive in watercourses during construction, the range of solutions for removal (or moderation) in both planned events and in emergencies; and to

3. provide background data for a short training course including

- the avoidance of water pollution,
- an overview of baseline work by IFE to date,
- a discussion of problems likely to be encountered during construction in relation to the Control of Pollution Act (COPA) and the Water Act,
- aspects requiring particular vigilance from environmental scientists,
- water pollution, prevention and clean-up procedures for both suspended solids and oil or diesel spillages,
- data on type and availability of booms, and
- making available suitable equipment and useful literature esp CONCAWE reports.

Objectives require that recommendations are made for the type, site and methodology of monitoring the water in watercourses with particular consideration to dissolved oxygen, suspended materials (or suspended solids) and discolouration together with their frequency as either short-term (or spot-sampling) or long-term monitoring ie. during the entire period that contractors are on-site. Recommendations and costs for suitable monitoring equipment which is easy to use and reliable are also required.

2.1 Recommendations for types of monitoring

If the Environmental Statement is to be implemented, it is necessary that both short-term or spot sampling of dissolved oxygen and turbidity are undertaken together with long-term monitoring at some sites of higher environmental sensitivity particularly at those at which wet construction is to be undertaken. Additionally, it is advised that a greater intensity of monitoring of dry construction sites is undertaken particularly near the start of such construction by each group of contractors to ensure that acceptable practices are being undertaken or constraints are being adhered to during work. Some background data has already been undertaken to determine levels during natural events (Dawson *et al* 1990, report RL9)

Suspended material can readily be observed as absent but is difficult to determine its concentration visually when present particularly if clays predominate. It is therefore necessary to use at least a portable instrument to determine if excessive levels are being input or caused to be suspended by for example rapidity of work rate of construction machinery or an unsuspected operation.

Dissolved oxygen is never obvious unless distressed fish are observed downstream of the construction site but at such a time critically low values of have already been established for some time; a chemical method or a correctly calibrated oxygen meter is therefore necessary.

2.1.1 Spot sampling

Dissolved oxygen and water turbidity should be monitored by environmental inspectors at an appropriate distance downstream eg from 50 -500 m downstream of construction when sites are visited. The level of 9 mg per litre (mg l^{-1}) of dissolved oxygen present in the contracts with

the construction companies relates to an arbitrary level below which construction can be required to cease. Realistic minimum levels ie critical for fish, are generally accepted to be 5 mg l^{-1} for salmonid fisheries and 3 mg l^{-1} for coarse fisheries. The difference between these two levels gives room for reasonable negotiation in discussing construction activities or work rates and makes due allowance for any effect of temperature or error in measurement of dissolved oxygen which may occur. Thus a reasonable mid-point level of c 7 mg l^{-1} should be considered as indicative of incipient critical conditions for salmonid streams without submerged vegetation ie the majority of these crossed in the project. Daily or diel changes in dissolved oxygen occur in vegetated streams (or in lakes and their outfalls) as a result of photosynthesis and respiration by submerged plants. The extreme ranges of diel changes of dissolved oxygen in natural watercourses should be considered to be $5 - 17 \text{ mg l}^{-1}$ and to occur in mid to late summer.

2.1.2 Long-term or continuous monitoring

Continuous monitoring of dissolved oxygen and suspended material or solids should be undertaken using data loggers with suitable sensors, to ensure critical levels are not reached (or predicted to reach) during periods for which an environmental inspector was not on site (Appendix I). [In order to ensure that the company's image of ensuring that there is conformity to the Environmental Statement, this should be undertaken by an independent assessment team.]

2.2 Recommendations for sites requiring monitoring

Sites at which monitoring is likely to be necessary are those of high environmental quality, for example, those with bio-morphological scores above c 6 in table 2.2.1, these with high fishery interest (most of the large northern and Scottish rivers), those sites with high bed or bank instability (marked as 'St.' in Table 2.2.1, Carling 1990, report WI2) and wet construction river crossing sites ie those subject to open trenching. However it is recommended that some dry construction sites, particularly those early on the list of crossings by each group of contractors, should be monitored (see above) as dry construction may have effects equally detrimental to streams as wet construction.

Table 2.2.1 New graded recommendations for monitoring of dissolved oxygen and/or suspended material during construction (* = low priority; ** = medium; *** = high; **** = essential to monitor) at watercourse crossings (RVX No.) with kilometer points (from revision 2), National grid reference, proposed or probable construction method (W = wet; D = dry; B = bore, pipe-jack, etc.), IFE biomorphological survey scores (0-10) with special invertebrate sites (*, top grade sites in Report RL9), previous monitoring recommendation (m) and sites monitored (M), stability survey undertaken St. = Bank/bed stability survey;), Carling 1990 (report WI2), and reinstatement sensitivity with care requirements from reinstatement and summary report RL9, Dawson *et al* 1990.

(key: n/s = not seen; adj = adjacent to watercourse)

RVX No.	km point	Watercourse	National grid ref.	IFE		Rein- stat- ment need	Mon- itor ing sugg.	Const. nique	New Monit. Sugg.
				IFE	Biomor Score (0-10)				
1	.60	RIVER AVON	26/947 798	1	4 ²			W	
2	1.39	RIVER AVON	26/950 797	2	3 ⁴			W	
3	5.34	MANUEL BURN	26/963 768	3	3 ⁴			D	
4	6.34	CROWNERLAND BURN	26/959 763	4	5	5		D?	**
5	14.17	HARE BURN -piped		X	-			-	
6	14.35	RIVER AVON, @ AVONBR.	26/903 722	5	4	5		W	***
7	14.60	HOLEHOUSE BURN	26/904 723	6	4			D?	*
8	15.70	LINMILL BURN	26/912 717	7	6 ²	6		D	**
9	17.97	MAD BURN	26/918 696	8	4 ³			D?	
10	18.57	UN-NAMED TRIBUTARY OF BARBAUCLAW BURN	26/918 690	9	-			D	
11	19.38	UN-NAMED TRIBUTARY OF BARBAUCLAW BURN	26/914 682	10	6	7		D	*
12	19.88	BARBAUCLAW BURN	26/912 679	11	5			D	
14	20.55	BLACK MOSS BURN	26/913 671	13	5 ¹	7		?	
15	21.87	ditches		-				D?	
16	22.97	HOW BURN	26/916 653	14	1 ³			D?	
17	24.11	RIVER ALMOND	26/914 643	15	1 ⁴			D?	
18	25.03	UN-NAMED TRIBUTARY OF RIVER ALMOND AT GREENRIGG	26/910 632	16	5 ¹	5		D	
-	27.09	South Calder Water		n/s				?	

19	30.26 LINGORE LINN	26/906 586	17	-			D?	*
20	31.38 KITCHEN LINN	26/908 575	18	5 $\frac{1}{2}$ *	10		D?	*
21	32.75 DARMEAD LINN	26/911 562	19	5	5	M	D?	**
22	33.44 MARCH SYKE	26/912 555	201	ditch			D?	
-	37.04 Trib of ABBEY BURN	26/923 525	202	moist			D	
23	38.82 NETHERTON BURN	26/932 511	20	3 $\frac{1}{4}$	4		D	
24	38.94 MOUSE WATER	26/933 510	21	2 $\frac{3}{4}$ *	4	St. M	D	(***)
25	42.72 DIPPOOL WATER	26/961 490	22	3 $\frac{1}{2}$	10	St.	D	**
28	48.57 RIVER CLYDE	26/965 442	25	- *	10	St. M	J	(***)?
29	49.58 PETTINAIN BURN	26/966 434	26	3			D	
30a	51.57 Trib of BROW BURN	26/966 410	203	wet			D	
30b	52.02	26/966 414	a b	wet			D	
30	52.83 BROW BURN	26/966 405	204	wet			D	
-	54.13 Trib of GLADE BURN	26/966 393	205	dry			D	
31	54.50 GLADE BURN	26/966 385	27	7	9		D	****?
32	54.98 SPITTLE BURN	26/967 381	28	6 $\frac{1}{2}$ *	5	St.	D	**
	55.25 Unnamed BURN	26/966 378	205	dry			-	
33	56.61 Unnamed, Park Knowe	26/977 368	206	nf			D	
34	58.16 KIRK BURN	26/985 357	29	6	7		D	**
35	58.87 UN-NAMED TRIBUTARY	26/985 350	30	2			D	
	59.77 Unnamed BURN	26/984 345	208	moist			D	
	60.45 Unnamed BURN	26/977 333	209	wet				
36	61.12 LANIMER BURN	26/977 329	31	5 $\frac{3}{4}$	3		D	
37	62.18 GARF WATER	26/972 319	32	6	6		D	**
	64.99 DINGLE BURN	26/961 296	210	2 $\frac{1}{4}$			D	
38	66.70 ROBERTON BURN	26/949 287	50	5 $\frac{1}{4}$	8	M	D	***
39	67.19 LADYGILL BURN	26/946 282	51	5 $\frac{1}{2}$	7		D	**
40	69.96 DUNEATON WATER	26/933 260	52	3?		St. M	W	***
41	75.51 GLENGONNAR WATER	26/921 217	53	5 $\frac{1}{4}$	5	St. M	D	*** or/both
42	76.06 GLENCAPLE BURN	26/923 213	54	7 $\frac{1}{4}$	7	St. M	D	***
	80.07 Harry Burn		-				D	
43	81.15 ELVAN WATER	26/947 171	55	6 $\frac{1}{2}$	7	St. M	D	**
44	81.65 GLENGITH BURN	26/949 168	56	7 $\frac{1}{2}$	3		D	**
45	81.86 BABBING WELL	26/952 167	57	7 $\frac{3}{4}$			D	*
46	82.39 RIVER CLYDE, Elvanfoot	26/956 166	58	-	6	St.	W	***
-	83.84 Trib. of Clydes Burn	26/972 160	59	6 $\frac{1}{2}$	7		D	*
47	84.01 CLYDES BURN	26/98. 16.	60	6 $\frac{1}{2}$	9		D	**
-	84.75 CONNY CLEUGH	26/980 158	211	6+?			D	*
-	85.52 SMIDDY CLEUGH	26/981 156	212	6 $\frac{3}{4}$			D	*

48	85.67 CLYDES BURN/Moss Cl.	26/987 158	61	5 ¹ ₂	10		D	*
49	87.74 STOCK CLEUCH	26/993 162	62	7	9		D	*
50	or CLYDES BURN in LANG CLEUCH							
51	88.01 ALLER CLEUCH	36/005 161	63	5 ³ ₄			D	
52	88.11 CLYDES BURN	36/010 157	64	5			D	
53	89.49 FOPPERBECK BURN	36/015 149	65	7	9		D	**
54	91.25 REDSHAW BURN	36/032 140	66	7 ¹ ₄	7		D	*
55	91.42 Trib of REDSHAW BURN	36/032 141	213	(7)			D	*
56	92.40 MARCH BURN and/or	36/040 137	67A	6			D	*
57	93.18 ROWANTREE GRAINS						(D)	
58	93.68 HASSOCKWELL BURN	36/04. 13.	67B	8	9		D	*
59	94.54 RAECLEUCH BURN	36/047 117	68	4 ¹ ₄	8		D	
60	95.85 DEAD BURN	36/052 105	69	5 ¹ ₂			D	
61	97.02 BUSHELBECK	36/056 097	70	-			D	
62	97.92 BUSHELBECK	36/060 089	71	5	5		D	**
	103.60 Unnamed stream	36/074 040	214	5 ¹ ₂			D	
63	106.19 EVAN WATER (ANNAN)	36/094 023	72	6		St. m		***
64	- (MOFFAT WATER)	36/095 023	73	5 ¹ ₄		m		
65	107.17 HOWBECK GILL	36/102 016	74	-			?	
66	108.16 BELDCRAIG BURN	36/104 009	75	8			D	**
67	110.26 BRUNSTONE BURN	35/112 989	76	6 ¹ ₂	4	St.	D	**
68	111.61 COOMB BURN	35/116 976	77	7 ¹ ₄ *	6		D	**
-	112.61 WILLOWS BURN	35/117 973	215	3 ¹ ₂			D	
69	113.25 WAMPHRAY WATER	35/120 961	78	6 ³ ₄	8	M	W	***
-	114.01 Small stream		n/s				D	
70	115.90 un-NAMED TRIBUTARY	35/125 941	79	5 ¹ ₂			D	
	OF RIVER ANNAN AT							
	PLANTATION FOOT		..					
71	117.55 BACK BURN	35/119 916	80	7 ¹ ₄			D	*
	or LANGSIDE CLEUCH							
	117.80 Unnamed stream	35/119 915	217	5				
-	118.02 Unnamed stream	35/117 914	218	dry			D	
-	118.92 Unnamed stream	35/117 913	219	dry			D	
72	120.59 DINWOODY GREEN BURN	35/116 893	81	8 ¹ ₂	6		D	*
73	121.56 RYECastle BURN	35/118 885	82	9	9		D	***
74	122.65 UPPERCLEUCH BURN	35/121 875	220	6 ¹ ₂			D	*
75	124.14 GREEN BURN	35/131 864	83	5	8		D	
76	125.10 DRYFE WATER	35/137 855	84	5 ³ ₄		St. M	W	***

77	126.00 UN-NAMED TRIB Dryfe W.	35/145 851	85	pipd			?	
78	126.36 KIRK BURN	35/148 851	86	6			D	
79	129.07 SLODAHILL BURN	35/161 831	87	4 ¹ *	10		D	**
80	129.70 CATLINS BURN	35/166 833	88	8	7		D	**
81	131.50 WATER OF MILK	35/182 823	89	7	9	St. M	W	***
82	131.77 PERCEIVING BURN	35/190 815	90	8	12		D	**
83	133.34 COUTS CLEUCH	35/202 805	91	-			D	
	134 MAGGIE BURN	35/206 796	92	6 ¹	adj.		-	
84	136.10 GRAINHALL BURN	35/213 791	93	7 ¹	10		D	**
85	136.43 DARLAWHILL GRAIN	35/215 791	94	6 ³	5	M	D	**
86	137.40 STONEYBECK BURN	35/220 786	95	6			D	
87	139.19 WIZZEN GILL	35/234 774	96	3			D	
88	139.30 MEIN WATER	35/235 774	97	6	6		D	*
89	140.98 KIRTLE WATER	35/249 772	98	6 ¹	5	St. M	W	***
90	143.57 BLACK CLEUCH	35/271 759	99	6 ¹			D	*
91	144.03 REDSTONES BURN	35/273 757	100	4 ³			D	
	@ GALLHILLS FARM.							
92	144.37 UNNAMED BURN	35/273 757	101	-			D	
	@ GALLHILLS FARM							
93	144.80 UN-NAMED BURN ON	35/278 751	102	6 ¹			D	
	BRANTETH FARM							
94	145.73 BRANTETH FLOW	35/287 748	103	-			D	
	BURN							
95	145.87						D	
95A	145.99						D	
96	146.93 SMALLHOLME BURN	35/293 737	104	6			D	*
97	147.56 LOGAN BURN	35/294 733	105	5			D	
98	149.64 LOGAN BURN	35/309 718	106	6 ¹			D	*
	150 ditch			u/c				
99	150.84 CAT SIKE	35/319 711	107	6 ¹			D	*
100	151.94 WEST GILL SIKE	35/331 715	221	3 ³			D	
101	153.38 RIVER SARK	35/343 719	33	7 ¹ *	8	M	W	***

102	154.34 BOG BURN	35/349 719	34	2 ¹			D	
103	154.96 BECK BURN	35/357 717	35	5 ¹		St.	D	
-	156.53 STREAM AT BATTEN BUSH	35/480 708	222	3 ¹			D	
104	158.30 RIVER ESK	35/383 693	36	6	10	St. M	W	****
105	158.35 WARREN BURN	35/490 694	223	6 ¹			D	*
106	160.94 HALL BURN	35/392 679	37	4			D	
-	161.45 SANDY SIKE	35/396 663	224	2 ³			D	

107	163.90 RIVER LYNE	35/398 651	38	54 ¹ *	7	St. M	W	***
-	164.88 Ditches Well Sike		n/s				D	
108A	167.33 ROCK CLIFFE BRANCH	35/410 619	39	12 ¹			D	
108B	167.48						D	
109	168.83 BRUNSTOCK BECK	35/417 606	40	4			D	
110	172.68 RIVER EDEN	35/437 578	41	44 ³ (7)	6	M	W	***
111	175.06 POW MAUGHAN BECK	35/443 557	42	64 ³	8	M	D	***
	@ NORTH SCOTBY							
112	175.92 POW MAUGHAN BECK	35/448 550	43	(5+)?			D	**
	@ SOUTH SCOTBY							
112A	176.75 POW MAUGHAN BECK	35/443 557	44	(4)?			D	**
	@ Cumnhinton							
113	177.17 Pow Maughan Beck		adj.				D	**
	180 Drains		n/s					
114	184.81 Pow Maughan Beck		n/s				D	
115	191.38 BLACKRACK BECK	35/490 420	46	24 ¹			D	
	192 Ditches / stream		u/c					
116	206.46 RIVER EAMONT	35/545 297	47	52 ¹ *	9	St. M	W	****
117	209.90 Light Water						D	
-	210.74 BULLS SIKE	35/548 258	225	-			D	
118	212.23 NOONHOWE SIKE	35/548 244	226	1			D	
119	214.64 RIVER LEITH	35/551 227	48	74 ¹	9	St. M	D?	***
	217 Gunnerkeld Sike		n/s					
120	220.23 TRAINRIGG SIKE	35/575 168	227	dry			D	(**)
121	222.02 TRAINRIGG SIKE	35/579 155	228	42 ¹ +			D	(**)
	224.77 Force Beck						D	
	228 Micklegill Beck		adj.				D	
122	232.09 BLIND BECK	35/610 063	110	NA			D	
123	232.50 BLIND BECK	35/613 066	111	NA			D	
-	232.58 BLIND BECK						D	
124	233 Trib of Chapel Beck						D	
125	233.55 CHAPEL BECK	35/620 057	112	LA 52 ¹	7		D	** or both
<hr/>								
126	233.61 RIVER LUNE	35/622 056	113	62 ¹ *	12	St. m	W?	***
	233 Tebaygill Beck		adj.					
	235 Tribs. (8) to R.Lune		u/c					
127	237.72 DRY GILL	35/613 019	114	72 ¹		m	D	**
	236 Tribs. (5) to R.Lune		n/s					
128	238.58 RIVER LUNE	35/612 011	115	NA	9	St. m	W?	***
	237 Bunces Gill & ditches		n/s					

	237	Tribs. (4) to R.Lune		n/s					
	238	Tribs. (5) to R.Lune		n/s					
	239	Trib. to R.Lune		n/s					
129	242.50	RIVER LUNE	34/624 981	116	NA	11	St. m	W?	***
-	242.49	FAIRMILE BECK	34/624 976	229	8 ¹ ₄		m	D	***
130	243.13	RIVER LUNE	34/624 972	117	NA	11	St. M	W	**** or/both
	243.	LOW GILL BECK	34/615 965	230	8 ¹ ₂		m		****
	244	Lambrigg Beck		n/s					
	246	Ellershaw Moss Beck		n/s					
-	250.17	STREAM AT KILLINGTON RESERVOIR	34/598 915	231	8 ¹ ₄			D	***
	248	small stream		n/s					
	250	Gillsmere Sike		n/s					
131	252.79	PEASEY BECK	34/585 896	223	9 ³ ₄ *			D	****
132	252.79	PEASEY BECK						D	****
	251	Drain		n/s				D	
133	254.30	trib of PEASEY BECK	34/580 880	233	7 ¹ ₄			D	**
134	256.74	FALL BECK	34/562 864	118	NA	7		D	**
135	257.99	Sillfield Beck		n/s				D	
136	258.38	Birks Beck		n/s				D	
137	260.14	HELLGILL BECK	34/553 835	234	9		m	D	****
138	261.00	ELMTREE GILL	34/533 751	120	NA			D	
	262	Canal Feeder							
139	262.52	FARLETON BECK	34/539 818	235	3			D	
	260	Beck at Atkinson Br.		n/s					
	268	Heron Syke		n/s					
	268	White Beck & ditches		adj.					
	271	RIVER KEER	34/528 719	122	4 ¹ ₂	10			*
	273	stream		n/s					
	277	DUNALD MILL BECK	34/522 678	236	dry				
	280	RIVER LUNE	34/515 648	123	4 ³ ₄		m	W?	****
	285.64	Trib of DENNY BECK	34/505 636	237	moist			D	
	285	stream		n/s					
	288	Blea Tarn Reservoir		adj.					
141	292.30	RIVER CONDER	34/495 567	124	5 ¹ ₄	8		W	**
142A	292.98	WHITLEY BECK	34/495 561	238	wet			?	
	293	ditches		n/s					
143	294.20	Trib of Whitley Brook		n/s				?	
-	296.35	Cocker Hall Water						?	

145	299.26 Brickworks watercourse								?	
146	299.55 Pad Syke								?	
147	299.69 RIVER COCKER	34/459 513	126	2					W	**
	300 LEA BROOK	34/463 492	127	-						
	300 LEA BROOK	34/462 490	128	-						
148	301.22 Crowleys Dyke								?	
150	304.07 Island Lane Drain								?	
151	308.31 PILLING WATER	34/463 431	130	-					?	
152	308.53 MOSS SIDE DRAIN	34/463 455	129	-					?	
153	309.55 RIVER WYRE	34/468 420	131	3 *	7		m	W	***	
155	310.40 RIVER BROCK	34/469 412	132	1 ¹ / ₂				W	**	
156	310.98 SOWERBY BROOK	34/469 445	133	NA	2			W		
157	311.53 INSKIP BROOK	34/465 434	134	NA				W		
158	314.14 INSKIP BROOK	34/466 377	135	NA				?		
	312 ditches		n/s							
	314 ditches		n/s							
159	320.07 SPEN BROOK	34/452 323	239d	-2 !				?	!	
	319 ditches		n/s							
	321 chanel's in marsh		n/s							
160	324.98 RIVER RIBBLE	34/465 281	136	-				B	(***)	
	322 ditches		n/s							
161	326.75 LONGTON BROOK	34/463 262	137	1				?		
162	327.89 TARRA CARR GUTTER	34/461 248	138	-				?		
	325 small ditch		u/c							
163	328.20 HALL CARR BROOK	34/461 247	139	1 ¹ / ₂				?		
164	329.71 RAKES BROOK	34/460 233	140	NA				?		
165	331.50 CARR BROOK	34/462 216	141	NA				?		
167	333.91 BRETHERTON EYES	46. 20.	142	NA				?		
	DRAIN									
168	334.65 EYES LANE DRAIN	34/471 195	143	NA				?		
169	334.98 RIVER YARROW	34/474 187	144	NA	8	St.		W	**	
170	335.58 COTTAGE LANE DRAIN	34/474 182	145	NA				?		
171	335.90 FINNEY LANE DRAIN	34/474 173	146	NA				?		
172	336.00 GREEN LANE DRAIN	34/475 166	147	NA				?		
173	336.64 MAWDSLEY MOSS DRAIN	34/473 160	148	NA				?		
174	337.15 MAWDSLEY MOSS DRAIN							?		
175	337.73 MAUDSLEY MOSS DRAINS	34/472 157	149	NA				?		
176	338.57 Old Reed Brook							?		
177	339.10 RIVER DOUGLAS	34/468 149	150	0		St.		W	*	
178	339.54 WHAM DITCH	34/467 145	151	(4)				?		

179	340.87 WHAM DITCH WEST	34/465 132	152	4			?	
180	337 ditches		n/s				?	
181	342.91 HOSCAR BROOK 1	34/464 120	153	(4)			?	
181	343.12 HOSCAR BROOK 2			(4)			?	
181A	347.10 SEFTON BROOK	34/445 078	240	2 ³ ₄			?	
	344 Dungeon Brook		adj.					
182	355.19 RAINFORD or Barkers Br	34/469 016	154	3			?	
183	355.94 Rainford Brook							
	353 ditches		n/s					
184	358.16 PASTURE LANE BROOK	33/482 995	155	-			?	
185	359.77 RAINFORD BROOK	33/491 991	156	(1 ¹ ₂)			?	
186	362.92 BLACK BROOK	33/522 989	157	2			?	(**)
186A	364.19 THE GOYT	33/553 988	241	4 ³ ₄			?	(**)
	362 stream		n/s					
-	367.30 CLIPSLEY BROOK	33/559 983	242	dry			?	
187	370.67 ELLAM'S BROOK	33/578 971	158	0			?	
188	373.66 SANKEY BROOK	33/558 949	159	(1 ¹ ₂)		St.	?	**
189	376.07 BURTONWOOD BROOK	33/550 915	160	NA			?	
190	378.76 WHITTLE BROOK	33/545 896	161	2 ¹ ₄	1		?	
192	380.92 PENKETH BROOK	33/547 880	163	1 ³ ₄			?	
193	381.82 BURROWS GREEN BROOK	33/548 876	164	(1 ¹ ₄)			?	
195	383 CANAL DRAIN	33/558 862	166	NA			?	
196	383.92 RIVER MERSEY	33/560 860	167	NA			B	(**)
194	385.25 MOSS SIDE BROOK	33/460 855	165	(2?)			?	
197	385.76 Keckwick Drain		adj.				?	
	386 stream		n/s					
-	386.84 Canal Drain		n/s					
	390 Trib. of Keckwick Br.		u/c				?	
198	392.71 KECKWICK BROOK	33/575 797	168	6+	9		?	***
198A	394.71 LONGACRE BROOK	33/579 783	243	4 ¹ ₄			?	
199	401.29 RIVER WEAVER	33/526 791	169	NA			W	
200	401.76 SHIP STREET COURSE	33/522 789	170	NA			?	
201	402.39 THE LUM	33/515 789	171	NA	4	St.	?	
204	403.21 BROOK FURLONG	33/510 789	172	NA			?	
205	407.05 HOOLPOOL GUTTER	33/474 776	173	0			?	
206	408.00 WESTCENTRAL DRAIN	33/465 773	174	5 ¹ ₄	4		?	*

2.3 Recommendations for monitoring methodology and equipment

Spot sampling to be undertaken by environmental inspectors are more likely to be undertaken using straight-forward hand-held instruments and which are readily available; these should be calibrated regularly at base (eg every 7-14 days, Appendix I & III). This type of instrument varies in precision, accuracy and stability but with reasonable care and understanding, they can provide reliable and adequate results within the requirements of the contracts or the limitations of site visits.

2.3.1 Dissolved oxygen in natural freshwaters

The concentration of dissolved oxygen can be measured using two main methods, dissolved oxygen electrodes and chemically using the the Winkler method or one of its modifications. The most convenient method is to use a calibrated oxygen meter and electrode or combination meter, of which there are many on the market (Appendix I, A1.1-A1.5). These electrodes are not considered to be as accurate as the chemical methods but because of their ease of use, they are recommended in most field situations.

There are a number of chemical field kits for measuring dissolved oxygen (Appendix I, A1.6) and although they are more time consuming than the electrode method they are still convenient and simple to use. If very accurate dissolved oxygen values are required, then special glass bottles with ground glass stoppers should be used, manganous sulphate and Winkler's reagent added in the field and the samples brought back to the laboratory for accurate titrations to be made.

In all sampling procedures care must be taken that:

- (a) the sample is representative of the water body being sampled, and
- (b) for the chemical methods, that the stoppered bottles must be filled very slowly or water must be collected in a special device to allow the sample bottle to be rinsed out at least twice to avoid the entrainment of air bubbles.

Calculation of dissolved oxygen concentration. Corrections have to be made for temperature and pressure corrections (incl. altitude effects) because the solubility of oxygen in water varies with these variables and to a smaller extent with others such as total dissolved solids and relative humidity (Table 2.3.1 & 2.3.2).

Equipment. There are several sensors available ranging from those with separate sensor and meter to combined ones for single-handed use; the latter are modest in cost and at least two have exchangeable sensor-heads for the measurement of dissolved oxygen, water acidity or pH and total dissolved solids or conductivity (Appendix I). Full use should be made of pre-prepared calibration solutions, although a beaker of fresh soft tap-water which has been aerated by an aquarium pump for 30-60 minutes provides an excellent standard suitable for spot samples.

Long term monitoring of dissolved oxygen requires considerable care in the choice of equipment, regular maintenance of logger and probes and is perhaps best undertaken by a specialist team with responsibility limited to this task. The cost of monitoring equipment for a few months use must be considered high, particularly if graphical output is required (Appendix I A1.8).

2.3.2 Suspended solids, suspended material or turbidity in watercourses
Suspended material and general discolouration is best measured using a single beam infra-red or dual beam visible suspended solids or turbidity sensor (Appendix I A1.7). These instruments measure the changes in intensity of a beam of irradiance causing changes in the output of a detector which relates to the amount of suspended solids present in the water. A calibration curve must be constructed for the relevant sensor by determining the response to various dilutions of a Formazine Turbidity Standard (FTU or other units including NTUs). The sensor must be protected from direct sunlight during spot sampling and calibration.

Full use should be made of pre-prepared calibration solutions.

2.3.3 Data logging equipment

Suitable equipment is likely to be battery powered and housed in environmentally resistant containers capable of occasional submersion but these requirements are not easily available or are relatively expensive (c £5000). Typical commercial equipment is not always reliable especially in continuous cold or wet conditions whereas other commercial installations require to be mains powered in near permanent installation eg huts etc. It is unusual for sets of suitable to be readily available and tested for aquatic conditions. (Appendix I).

Table 2.3.1 *Solubility of oxygen in distilled water in equilibrium with air at normal pressure (760 mm Hg) and 100% relative humidity (from Montgomery, Thom & Cockburn 1964; closely similar values are given by Carpenter 1966 and Murray & Riley 1969)*

Temperature of sample ° C	C_s Solubility mg l ⁻¹ μmol l ⁻¹		Temperature of sample ° C	C_s Solubility mg l ⁻¹ μmol l ⁻¹	
0	14.63	457	18	9.46	296
1	14.23	445	19	9.27	290
2	13.84	433	20	9.08	284
3	13.46	421	21	8.91	278
4	13.11	410	22	8.74	273
5	12.77	399	23	8.57	268
6	12.45	389	24	8.42	263
7	12.13	379	25	8.26	258
8	11.84	370	26	8.12	254
9	11.55	361	27	7.97	249
10	11.28	352	28	7.84	245
11	11.02	344	29	7.70	241
12	10.77	337	30	7.57	237
13	10.53	329	31	7.45	233
14	10.29	322	32	7.33	229
15	10.07	315	33	7.21	225
16	9.86	308	34	7.09	222
17	9.65	302	35	6.98	218

The saturation concentration (C_s) at the temperature at which the sample was taken may be found from Table 2 by interpolation. Then if the actual concentration of oxygen in the sample is found by analysis to be C , the percentage saturation is given by $100 \times C/C_s$.

Table 2.3.2 *Correction factors for altitude (from Mortimer 1956)*

Altitude (m)	Correction factor	Altitude (m)	Correction factor
0	1.00	1300	1.17
100	1.01	1400	1.19
200	1.03	1500	1.20
300	1.04	1600	1.22
400	1.05	1700	1.24
500	1.06	1800	1.25
600	1.08	1900	1.26
700	1.09	2000	1.28
800	1.11	2100	1.30
900	1.12	2200	1.31
1000	1.13	2300	1.33
1100	1.15	2400	1.34
1200	1.16	2500	1.36

3 SOURCES, MODERATION AND PREVENTION OF SUSPENDED MATERIAL
 IN WATERCOURSES

Concern has previously been expressed over the effects of sediments moving downstream as a result of construction activities where pipelines cross rivers and stream (Dawson 1989). Previous surveys have highlighted the need for pre-construction monitoring of suspended material and diel oxygen changes in the same season of the year prior to pipeline construction at selected rivers and streams, to determine the potential effects and to establish baseline levels. Excursions in levels caused by natural events ie spates and floods, are particularly important and these have been already been undertaken to give a framework by which to judge the effects of construction.

The effects of sediment settlement on fish populations especially spawning and development, has already been restricted by the choice of undertaking work between March, now May, and October (Welton 1990a, Report RL3 Scotland; Welton 1990b, Report RL5 England) and also by construction techniques by negotiation with the relevant river authority.

The potential impacts of elevated suspended material levels directly or accidentally include:

- (1) the modification of habitat by the effect on biota of elevated suspended solid concentrations passing and settling downstream increasing abrasion, clogging respiratory surfaces and by the settlement of suspended material affecting invertebrate feeding and fish spawning;
- (2) the reduction in dissolved oxygen brought about by the respiration of suspended organic matter as it passes down stream and which could result fish kills in particular;
- (3) the indirect effect of the reduction in light penetration due to increased water turbidity and the subsequent reduction in photosynthetic rates of submerged macrophytes where present; and,
- (4) the visual impact and downstream passage of sediment plumes.

Baseline levels of suspended material and dissolved oxygen resulting from natural events ie. spates and floods, are being established from data collected at several of the selected construction sites (Dawson et al 1991 report RL9).

3.1 Sources of suspended material

Previous experience indicates that varying types of bed, bank or trench material may enter the water and move downstream directly from the stream bed but also from back-cutting into the banks, directly from the main running trench, from various dewatering or pumping procedures (authorized or not) and accidental discharges. In view of the moderate to high gradients of a large part of the route, the runoff, capture and accumulation of water in the running trench is likely to be large even during normal rain events; this silt-laden water will obviously accumulate at the lowest points ie the rivers and streams and is likely to provide a potential and catastrophic input of suspended material to watercourses.

Finer materials travel further than coarser ones of the same density and indeed very fine clays may not settle at all and pass to the sea. Organic materials eg peat, of the same size, being considerably less dense, take significantly longer to settle but are less common in rivers or their banks. The impact of materials suspended from construction activities is obviously related to the total quantity of materials passing from the construction area to settle on the stream bed. The finer fractions which disperse further (and their visual impact) are related to discharge and the rate of supply or construction work rate. Thus types of material, position and extent of excavation, water flow (velocity and discharge) and time period of construction and back-filling, are key factors in evaluating the potential impact. In addition, there does not seem to be any generally accepted definition of the lower limit of visual impact in terms of particle and concentration and this needs to be examined to meet NRA or River Purification Board requirements.

3.2 Recommendations for sediment control

Dry construction is only suitable for the smaller streams but its benefits can be spoilt by inadequate (or absent) provision either for filtration eg prepared filter units or even through hay bales, or alternatively, settlement tanks of the silt-laden water pumped from ditches (which are advised here). The choice between the use of pipes sealed to the natural stream banks or the use of pumps to transfer water across the pipeline trench is not always clear but the former is generally advised here. In other studies, the failure to make adequate use of data available on discharge to provide adequate pumping capacity can result in partial or total failure of otherwise good planning.

Wet construction is considered the most economic solution for large rivers but is only suitable provided that adequate pauses are included in the work programme, or when there is submerged aquatic vegetation present that only daytime working is undertaken. The suspended solids loading of the river should be measured in rivers with salmonid fisheries to ensure adequate control of sediment loading are being adhered to. On-site advice is advocated for the majority of sites and as is the predictive modeling of the downstream sediment plumes.

The major source of fine material to be expected is during the back-cutting of the main trench by some 3-10 m into both river banks; this could be minimised by greater care in bank removal or some isolation using piling during this phase of construction. Some fine material will arise from bed materials during construction of the main trench across the river however it seems likely that the gravels are well worked in these rivers and contain little fine material (Dawson *et al* 1991, report RL11). It is uncertain if this assumption applies to the deeper layers as borehole logs from either bank indicate are only descriptive with no sieve analysis being provided.

The main running trench should be dewatered through portable settlement tanks, or by the construction of settlement channels or lagoons, which should be sufficiently large to contain the considerable volumes of water to be expected both from normal drainage and from rainstorms. The use of simple filters, eg straw bales, may be sufficient in normal circumstances but they must be provided with adequate support to avoid movement when fully dammed by water. The best advice is to avoid the development of difficult situations by rapid in-filling of the running trench and by the provision of regularly spaced diversionary holding for water areas away from watercourses.

4. WATER POLLUTION, PREVENTION AND CLEAN-UP

4.1 Water pollution law

EC Directive 85/337/EEC- Assessment of the effects of certain public and private projects on the environment (effective from July 1988).

This made environmental assessments mandatory for certain projects and discretionary for others including pipelines. The minimum requirements of this are laid down in Article 5.

The electricity and pipeline works (assessment of environmental effects) [SI No.442, 1990 (update of SI 167, 1989)].

This was introduced to implement the above Directive (85/337/EEC) in the UK with respect to pipelines. It applies to cross-country pipelines (and power stations) which require authorization under the Pipelines Act 1962.

Under SI 442 the developer can seek the opinion of the Secretary of State as to the need for an environmental statement (ES, a report on the likely environmental consequences of a project). However, The Pipelines Inspectorate of the Department of Energy are unlikely to grant a Pipeline Construction Authorization (PCA) without first studying some form of ES. The general contents of an EA are described under Article 3 of the EC Directive (85/337/EEC) and have been discussed further by Hadley (1991) and Ryder (1989).

Water Act 1989 [replaces Part II of the Control Of Pollution Act (COPA), 1974].

Any works involving a river ie., bridge building, pipe laying etc requires a land drainage consent.

Part III, Chapter I of the above Act is concerned with the control of pollution with the National Rivers Authority (NRA) being responsible for this.

s.107(1)(a) "...It is an offense to cause or knowingly permit any poisonous, noxious or polluting matter or solid matter to enter any controlled waters..." There was a loophole concerning solid matter in COPA.

s.107(1)(e) "...any matter whatever to enter inland waters so as to tend (either directly or in combination with other matter which he or another person causes or permits to enter those waters) to impede the proper flow of the waters in a manner leading to or likely to lead to a substantial aggravation of pollution due to other causes, or the consequences of such pollution.."

s.109(1) "...an offense is committed if, without the consent of the Authority, a person removes from any part of the bottom, channel or bed of any inland waters a deposit accumulated by reason of any dam, weir or sluice holding back the waters , and does so by causing the deposit to be carried away in suspension."

s.109(2) " Also it is an offense if, without consent, a person causes or permits a substantial amount of vegetation to be cut or uprooted in any inland waters, or to be cut or uprooted so near to those waters that it falls into them, and fails to take all reasonable steps to remove the vegetation."

The general view is that controls on pollution arising through deposits and disturbance of vegetation will be tightened.

Other related Directives/ Acts:

EC Directive 76/464/EEC- relating to dangerous substances discharged to the environment.

EC Directive 78/659/EEC- relating to quality of freshwaters to support fish life.

Town and country planning (assessment of environmental effects) regulations 1988 (SI No.1199).

Environmental Assessment (Scotland) regulations 1988 (SI No.1221).

Town and country planning (assessment of environmental effects) (amendment) regulations 1990 (SI No.367).

4.2 Behaviour of oil spills

The aim of the following is to provide an outline of the principle methods which may be employed to prevent or clear up potential accidental oil spills during river crossing phases of the construction programme. In this context the notes are restricted to spills involving vehicle fuel and lubrication oils and to those occurring on or near to rivers. It is assumed that the volumes of oil involved will be relatively small. [Information on other types of oil spills including large volume spills, ones where ground water contamination may occur etc., or more details on any of the methods are given in CONCAWE reports 7/81 & 10/83 and on manufacturers in the list in (Appendix II).]

4.2.1 Behaviour of oil spills

On soil

Oil spilled during river construction operations is likely to run over the ground before it reaches a water course. The extent to which the oil will penetrate the soil will be determined by the type and nature of the soil, the position of the water table relative to the ground surface and the volume and type of oil (Figure 4.2.1).

Due to agricultural porosity, worm holes etc., the oil will usually saturate the top 10-20cm of the soil. Obviously, penetration will be greatest in puddles formed in dry hollows (if the hollow contains water penetration will be prevented).

[The volatile components will evaporate presenting an explosion risk. The duration of this will depend on the product, volume spilt, ambient temperature, wind conditions and amount of spreading. An explosimeter can be used to determine if the vapour is flammable.]

In the subsoil

Oil penetrating the subsoil will move downwards under the influences of gravity and capillarity action. The size and shape of the resulting oil body will depend on the nature and structure of the soil, the position of the water table and upon the type and quantity of the oil (Figures 4.2.2 & 4.2.3). In fissured rock, oil will move relatively quickly along the course of the fissures. The downward progression may be stopped if:

- i) an impermeable layer is encountered.
- ii) the water table is reached.
- iii) the threshold of 'residual saturation' is reached.

Figure 4.2.1 Extent of oil penetration of soil in relation to type or nature of soil and viscosity of oil.

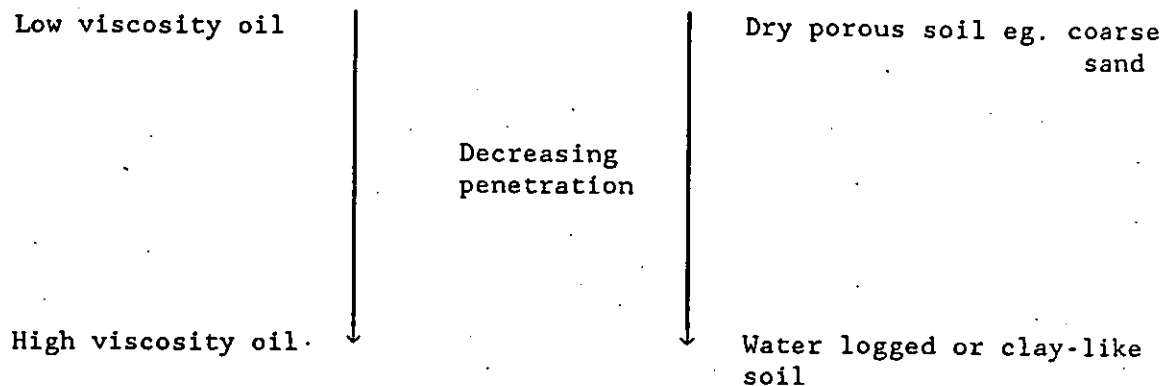


Figure 4.2.2 Generalized shapes of spreading oil bodies (from CONCAWE 7/81).

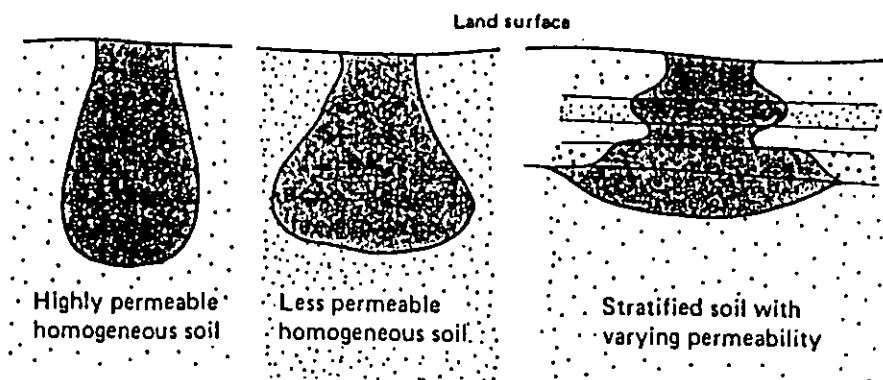
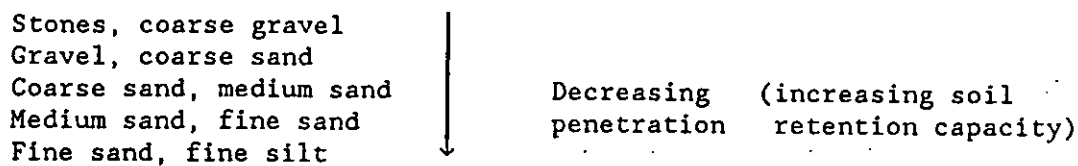


Figure 4.2.3 Depth of oil penetration in relation to substrata type.



On surface water

An oil film as little as 4×10^{-5} mm can be visible to the human eye and this is equivalent to 40 litres of oil spread over 1 km^2 (Table 4.2.1).

Most oils will rapidly spread to form a thin film of about 1mm. Dirty polluted water may inhibit spreading creating a final thickness of around 1mm. Viscous oils (especially heavy fuel oils) spread out to a lesser extent and if the ambient temperature is low they can congeal as fairly large lumps.

Evaporation of the lighter fractions will begin on release of the oil so presenting a potential explosion risk. The time taken for this to pass will be determined by the ambient temperature, oil type and volume, the thickness of the oil layer and wind speed.

On fast turbulent streams, agitation of the water-oil interface can result in the formation of stable water-in-oil emulsions which because of their increased volume and viscosity are more difficult to clean up.

In sheltered stretches oil will achieve the same velocity as the water surface. Where the river is exposed wind action will also influence oil movement and may be helpful by concentrating the oil on one side of the river.

Table 4.2.4 Oil film appearance vs. quantity (from CONCAWE 7/81):

Appearance of film	Approximate film thickness		Approximate quantity of oil for film	
	10^{-6} in.	10^{-6} m. (microns)	Imperial gallons per mile ²	Litres per km ²
Barely visible under most favourable light conditions	1.5	0.04	25	44
Visible as a silvery sheen on water surface	3	0.08	50	88
First trace of colour may be observed	6	0.15	100	176
Bright bands of colour	12	0.3	200	351
Colours begin to turn dull	40	1	666	1168
Colours are much darker	80	2	1332	2337

4.3 Containment, removal and reclamation of oil spills

Oil spill response equipment capable of at least containing any spilt oil should be on hand during all aquatic crossings. Staff fully trained in emergency response procedures and familiar with all equipment should also be on site during operations. [Several of the manufacturers listed in Appendix II offer emergency pollution response courses although training may be available 'in-house' through Shell UK]

Close liaison with relevant emergency services (NRA, Water Companies, Fire service etc) will be necessary to formulate (and update) emergency procedures and to ensure a rapid coordinated response to any incident.

4.3.1 Soils

Many of the rivers to be crossed are environmentally sensitive sites containing important fisheries and/or are used for public water supply (either directly or indirectly). Consequently everything possible should be done to prevent any spillages from entering adjacent water courses. Additionally, clean up operations on soil are normally easier than on water.

For relatively small spills the use of sorbent materials will usually be sufficient to contain the spreading oil. These are available in several forms (eg., pads, pillows, mats and blankets: see Appendix II) to suit particular applications. During 'high risk' operations such as the refueling of vehicles it is recommended that sorbent materials capable of coping with any potential spills are laid around vehicles. Soil, sand or sorbent dams may also be used to prevent oil from entering water courses.

Sorbents may also be employed for the removal of small volumes of oil. For larger volumes pumps should be used preferably fitted with strainer or suction nozzles. Puddles may also be removed using portable pumps or alternatively using sorbent mops. The final choice of removal equipment will also be determined by the type of oil, the substrates porosity and condition and distance from watercourses.

Although the use of chemical surfactants to aid recovery is not recommended, non-toxic bacterial biosurfactants are now commercially available which are capable of aiding recovery or degrading the oil and may be of use in certain circumstances (eg. Archaeus Technology Group).

Recovered oil may be kept in portable storage tanks (eg., prefabricated rigid tanks, polyethylene pillow or sausage tanks) prior to final removal. If large volumes of oil are involved the construction of imperviously lined pits may be necessary.

Reclamation from soil

Oil in the soil tends to damage plants by inhibition of water and nutrient uptake rather than direct toxic effects although some will contain lead. Residual concentrations may be tolerated by established plants in coarse soils but even low levels may adversely affect certain seed germination.

Following most spills naturally present hydrocarbon degrading bacteria will be able to restore the soil to a usable condition within 1-4 years subject to the nature of the oil, nutrient and oxygen availability and ambient temperatures, and provided that the temperature does not fall below 7°C (CONCAWE 7/81). To enhance this natural recovery the following techniques may be used:

- i) aeration eg., by tilling, ploughing etc.
- ii) dilution of the oil content eg., by mixing soil
- iii) fertilization eg., by the addition of NPK fertilizers
- iv) bacterial seeding (eg. Archaeus Technology Group).

Affected river banks are preferably cleaned by the physical removal of contaminated substrata for proper disposal. This also applies where the quantity of oiled soil is small, or in very sensitive locations, where the physical removal and replacement with clean soil will be a viable option.

4.3.2 Watercourses

Spills will often run over the ground before reaching a watercourse. Partial evaporation will occur and what is left will probably be contaminated with silty sediments (this is especially the case with the project where adjacent soils will have been disturbed by construction activities). Consequently the density of the oil will be increased and it will not rise so easily to the water surface. Longer time is therefore needed for the oil to separate and this should be taken into account when positioning oil containment or removal equipment.

Containment

All containment devices work on the principle of creating a barrier to oil movement at surface level. By containing the oil the barrier will also concentrate it into a thicker layer thereby making final recovery easier.

On small turbulent water courses where the use of booms is not practical, emergency earth or sand bag dams can be rapidly constructed to hold the oil. These should be located where there are high upstream banks to allow for the increased water depth. Water can be pumped from the bottom of the water course and discharged downstream if the dam is likely to be overtopped. Discharged water should preferably be pre-filtered (eg., through straw bales) and careful positioning of the return pipes to prevent erosion of the bed or banks will be needed (possibly by pumping water into a flexible tank with an overlapping base-plate on the water course bed).

Alternatively pipes may be inserted towards the bottom of the dam to allow the passage of uncontaminated water with care again being taken to prevent erosion by discharging water.

Containment and removal in small ditches is probably best achieved by the use of sorbent materials eg. pillows and booms (see Appendix III) although sand bagged and 'spade' dams may also be of use. Spade dams usually consist of a metal plate (mild steel or aluminium) that can be hammered into the ditch with the edges cutting into the banks to provide a water-tight seal. If the free passage of uncontaminated water is required a gap can be left at the bottom of the dam or pipes incorporated into its design

For larger water courses oil confinement will mainly involve the use of booms. Two basic boom designs are generally available:

i) Fence booms: these consist of rigid or semi-rigid material which forms a vertical screen against the flow of oil. Buoyancy is provided by low density plastic filled compartments or plastic foam blocks. Ballast usually consists of weights attached to the screen base. The different components of the boom normally have to be assembled on site.

ii) Curtain booms: these consist of long buoyancy tubes with a pendant skirt with ballast weights at the base. Curtain booms are often air inflated and so they tend to be less bulky than fence type booms. They are also generally easier to set up although some kind inflation mechanism is required.

Curtain type booms appear to perform better than fence booms under high current conditions and this together with their relative compactness and quicker deployment times probably make them more suitable for use in potential applications (see Appendix II)

Another type of boom applicable to inland spills is constructed from lengths of sorbent material which are oleophilic and hydrophobic (eg., polyurethane plastic foam). These are normally employed for removing the last traces of oil on enclosed or sheltered waters and it is doubtful they will perform well in fast flowing and/or turbulent streams due to their low draught (the submerged section of the boom). However when used in conjunction with conventional booms or where currents are low they provide efficient recovery systems for small spills. Sorbent booms are available in a number of forms many of which can be cut or joined to achieve the desired length (see Appendix II).

When deploying booms speed is essential and it is advisable to position booms prior to any engineering work at ecologically sensitive sites or where high risk construction techniques are in operation. At the very least booms (and other clean-up equipment) should be positioned at suitable bank side locations to enable rapid deployment by trained personnel.

Factors which need to be considered when selecting boom sites include;

- i) Prevailing wind conditions - should be towards collection points.
- ii) Water velocity - areas of low water velocity should be chosen, especially near banks.
- iii) Water turbulence- a relatively undisturbed area upstream is desired to allow oil to rise to the surface.
- iv) Water depth- must be sufficient to operate removal equipment.
- v) Good access- preferably allowing vehicles.

Boom positioning within the river or stream must also be considered. If it is merely placed at right angles to the current then oil will begin to under-pass the boom once the velocity has reached 0.3 m s^{-1} . This would be reduced to 0.15 m s^{-1} if the water was only twice the depth of the boom draught. Where velocities are high, boom performance can be enhanced by positioning the boom at an acute angle to the flow. For practicalities of boom length required, 14° is normally taken as the finest angle between the boom and flow (Wardley-Smith, 1983). These chevron boom arrangements have successfully been used in currents up to 1.2 m s^{-1} .

In all cases an effective seal must be created between the bank and the boom eg., by positioning an extra length of boom along the bank upstream of the main boom.

Wind and current conditions must also be taken into account when considering mooring requirements eg., intermediate anchors may be needed. To prevent small pockets or 'cusps' of oil forming along the boom length parachute type multiple mooring arrangements are recommended. At least a 50% safety margin should be allowed for when estimating loading forces on booms.

Summary of boom deployment recommendations:

- Prevailing current and wind conditions should be carefully considered.
- Boom length should be a minimum of 1.5 times the river width.
- Intermediate mooring desirable in currents $> 0.3\text{m s}^{-1}$.
- Boom length should be a minimum of 2 times the river width where the current exceeds 0.6m s^{-1} (and preferably up to four river widths).
- Floating booms can be used in currents up to 1.2m s^{-1} .
- Deploy in a smooth curve without cusps at an acute angle to the current.
- Mooring rope length should be a minimum of five times water depth.
- Submerged height should not exceed 20% of the water depth.
- An extra section of boom should be used to form a seal at the bank and provide an auxiliary boom.
- Manufacturers operating instructions should be followed closely.
- Water depth should be sufficient to enable the efficient use of oil removal equipment.
- Good access (preferably vehicular) should be allowed for.

Recovery of contained oil

For minor spills the use of sorbent materials in conjunction with booms should be sufficient for adequate oil recovery. Sorbents are now available in a variety of forms including loose strips, pads, pillows, bales, mops as well as complete booms.

Sorbent retrieval tends to be labour intensive involving hand operated rakes and scoops. Disposal of large quantities of contaminated sorbent may create problems although many are now re-usable to a certain extent.

For larger volumes of spilt oil the use of skimmers (mechanical devices for the collection of oil) will be necessary prior to final oil recovery. The two main types of skimmers applicable to the project are described below:

i) Sorption skimmers: these rely on an oleophilic or hydrophobic material to recover oil from the water surface. The adhesive or sorptive surface is usually in the form of a spinning disc or a flexible belt or rope with the oil being removed from the surface by either a wiper blade (disc skimmers) or a pressure roller (belt or rope skimmers).

Disc skimmers can be used on a wide variety for the recovery of a wide range of oil viscosities (and emulsions) but are most efficient for oils of moderate viscosity. Belt or rope skimmers appear to work best for light to medium oils depending on the sorptive material chosen.

ii) Weir skimmers: these work by allowing oil to flow over the rim of a weir into a container where the liquid layer is maintained at a lower level by pumping. Reasonably accurate alignment of the rim is necessary to avoid collecting large volumes of water with the oil (increasing pump size required and creating oil-water separation problems).

Weir skimmer recovery rates are inhibited by high viscosity oils which will not flow freely into the weir. Additionally recovery falls off rapidly at low oil film thickness although this problem may be overcome by removing both oil and water and subsequently allowing these to separate in a suitable container before returning decontaminated water to the river. Floating weir skimmers are not recommended for use in currents above 0.3 m s^{-1} . (for skimmer manufacturers see Appendix II)

4.4 Recommendations for the prevention of pollution during re-fueling operations

It is recommended that

1. re-fueling operations are not undertaken in proximity to water courses.
2. re-fueling should not be carried out on bridges whether permanent or temporary.
3. where re-fueling is necessary it should be within bunded areas of adequate design and capacity. Additionally sorbent materials should be laid around the vehicles or plant involved or at least on hand for rapid deployment in the event of a spill.
4. Strict procedures should be adhered to to prevent overfilling. These should include:
 - i) Good communications between delivery and receiving vehicles or plant.
 - ii) Means of rapidly shutting-off flow of fuel in an emergency.
 - iii) The use of accurate fuel gauges or dip sticks.
 - iv) Correct operation of valves (if applicable)
 - v) Regular checking of valves, joints, pipes, hoses etc for leaks and other defects.
 - vi) All staff involved in fueling operations should be fully trained in these together with associated emergency procedures etc. Fueling instructions should be prepared in concise non-technical language and should be displayed in a visible place.
 - vii) The fuel capacity of the vehicle or plant fuel tanks should be clearly marked by their filler caps.
5. Following delivery all valves, fuel caps etc should be properly closed. Any oil dripping from pipes or hoses should be collected in a tray or other suitable container preferable in a sorbent material and disposed of correctly.

5 RECOMMENDATIONS

It is recommended that

1. environmental inspectors (or others) should, when visiting watercourse crossing sites, make spot measurements of dissolved oxygen and water turbidity downstream of construction ;
2. wet construction watercourse crossing sites should be continuously monitored during the entire period of construction for dissolved oxygen, and suspended materials (or suspended solids) and/or discolouration, to provide data and to ensure adherence to contracts and to company environmental policy. Sites, as outline in Table 2.2.1, broadly include all of the larger wet crossing sites, except those with minimal established environmental value; together with
3. a reduced set of the more sensitive dry construction sites should also be monitored (as 2. above) including particularly those with high environmental quality, examples of dry construction at sites early in the work programme of each group of contractors to establish that good working practices are being applied, and those
4. sites with more unstable banks, beds or with special features, monitored particularly for suspended material.
5. dissolved oxygen and/or suspended material should be monitored at several sites, these have been prioritized and number, dependant upon the number of bore crossings, approximately 8 sites at which monitoring is essential, 28 highly advisable, a further 38 which should be seriously considered and another 25 which could be monitored; the remainder, c100 are not considered necessary to monitor.
6. the potential sources of suspended material require either on-site determination with a care or awareness statement being produced for expected and emergencies and including methodology for the amelioration or prevention of suspended solid loadings to the watercourse before commencement of construction or
monitoring with immediate feed back to construction teams on such factors as excessive work rates, non-permissible operations especially pumping towards the watercourse, or expected effects of rainfall etc.

Data is also included for a short training course

1. on compliance with water pollution law,
2. on sensors suitable for spot sampling together with their calibration procedures, and the
3. on operation and range of equipment available for the prevention and clean-up of oil spills, etc.

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Appendix 1 List of suppliers and agents for monitoring equipment for dissolved oxygen, water temperature water turbidity and data loggers. (enboldened data indicates use by IFE)

A1.1 Oxygen, temperature and pH probe manufacturers or agents list.

BDH Ltd.
Broom Road
Poole
Dorset
BH12 4NN
(0202) 745520

Camlab
Nuffield Road
Cambridge
CB4 1TH
(0223) 62222

Ciba-Corning Analytical
Halstead
Essex CO9 20X
(0787) 475155

Clandon Scientific Ltd.
Lynchford House
Lynchford Lane
Farnborough GU14 6LT
(0252) 514 711

Eurisem Technics
40 High Street
Earl Shilton
Leics. LE9 7DG
(0455) 848 424

Fisons Scientific Equipment
Bishop Meadow Road
Loughborough
Leics. LE11 0RG
(0509) 231166

Grant Instruments
Barrington
Cambridge CB2 5QZ
(0763) 260811

Labmart (Cambridge) Ltd.
1 Pembroke Avenue
Waterbeach
Cambridge CS5 9QR
(0223) 861 665

Palintest Ltd.
Kingsway
Team Valley
Gateshead
Tyne and Weir
NE11 0NS
(091) 491 0808

Partech (Electronics) Ltd
Eleven Doors
Charleston
St Austell
Cornwall PL25 3NN
(0726) 74856

pHox Systems Ltd.
Ivel Road
Shefford
Bedford
SG17 5JU
(0462) 813 103

Solomat Mfg. Ltd
2 St. Augustines Parade
Bristol BS1 4XJ
(0272) 226561

Tintometer Ltd
The Colour Laboratory
Waterloo Road
Salisbury
SP1 2JY

A1.2 Combined dissolved oxygen, temperature and pH modular probes.

Manufacturer (Agent)	Model	Ranges	Resol- ution	Other features	Approx Price (£)
Ciba Corning	Checkmate	0-200% 0-20.0mg/l -5-100 C 0-14pH	1% 0.1mg/l 0.1 C 0.01pH	Conductivity / TDS module	c 250
Orion (Cole-Palmer)	L-05702-25	±199mV -5-105 C -2-19.9pH	1mV 1 C 0.01pH	Ion conc. kit available.	c 500

A1.3 pH meters (all record in the range 0-14pH) (Chemical kits and test papers are also available from most manufacturers and suppliers)

Manufacturer (Agent)	Model	Accuracy	Other features	Approx Price (£)
(Cole-Palmer)	L-05941-10	± 0.5pH	(disposable)	19
	L-05941-00	± 0.2pH	"	25
	L-05941-20	± 0.1pH	"	31
	L-58600-00	± 0.01pH	Temperature	245
Digi-sense (Cole-Palmer)	L-05830-00	± 0.01pH		75
	L-05985-80	± 0.01pH	Temperature	181
Eurisem Technics	EP721	± 0.01pH		67
	EP602	± 0.5pH		24
	EP605	± 0.02pH	Temperature	195
Knick (Labmart)	751	± 0.01pH	Temperature	210-255
	752	± 0.01pH	Temperature	276-320
Lilliput (Labmart)	750	± 0.1pH		220
	765	± 0.1pH		285
Palintest	PT105	±0.01pH	Temperature	149
pHox Systems	Series 21	± 0.01pH		
Schott (Camlab)	CG817T	± 0.01pH	Temperature	315
	CG818	± 0.02pH		225
	CG818T	± 0.02pH	Temperature	310
	CG728	± 0.1		220

A1.4 Hand held oxygen and temperature meters (all temperature compensated).

Manufacturer (Agent)	Model/ Cat. No.	Ranges	Accuracy	Features	Price (£)
Cole-Palmer	L-05505-00	0-19.99mg/l	±1.5% FS		290
		0-199.9 C	±0.2 C		
	L-05948-60	0-19.99mg/l	±2% FS		384
		0-200%			
	L-05513-55	0-199.9 C	±0.2 C		
		0-19.00ppm	±1.5% FS		247
Whatman	D0200	0-50 C	±1% FS		
		0-16ppm	±0.25ppm		235
		0-32 C	±1 C		
		0-19.99mg/l	±1.5%		

A1.5 Portable oxygen and temperature meters.

Manufacturer (Agent)	Model/ Cat. No.	Ranges	Accuracy	Features	Price (£)
Cole-Palmer	L-05946-70	0-15mg/l	±2% FS		
		0-120%			
		0-50 C	±2% FS		
	L-53100-10	0-60mg/l	±1% FS		
		0-199.9%			
Obisphere Labs	2609	0-50 C	±0.2 C		
		0-100 C	±0.2 C	Salinity compensation	795
pHox Systems	62TE 67		+1% FS		
		-5-40 C	+0.5 C		
Partech	5100	% and mg l ⁻¹			c 1200
YSI (Clandon)	50B	0-19.99mg/l	+0.03%		750
		0-199.9%	+0.2%		
		-5-45 C	+0.1 C		
	58	0-20.0mg/l	±0.03%	Salinity compensated	995
		0-200.0%	±0.3%		
		-5-45 C	±0.3 C		
	57	0-20.0mg/l	±1mg/l	Salinity compensated	785
		-5-45 C	±0.5 C		
	51B	0-15mg/l	±0.2mg/l	Altitude + salinity compensated.	485
		-5-45 C	±0.5 C		

A1.6 Field chemical test kits for measuring dissolved oxygen.

Manufacture (Agent)	Model	Range	Determinations	Price (£)
Aquamerck (BDH)	11107	0-40mg/l	~100	22
Hach (Camlab)	1469-00	0-12mg/l	~100	50
Lovibond (Fisons)	Comparator (WHT-HBC-570L)			100

A1.7 Turbidity meters (turbidimeters)

Manufacture (Agent)	Model	Range	Comments	Price (£)
Hach (Camlab)	Portalab (16800-00)	0-100NTU	Comparator style turbidimeter.	1070
Lovibond (Tintometer)	TM720	0-200NTU	As above	695
Orbeco-Hellige (Labmart)	965-10	0.01-1000NTU	may also be used for other tests eg., chlorine, nitrate	895
Palintest	2010 (PT280)	0.1-199.9NTU	Comparator style	220
Partech Inst.	DRT-15C 730 7000-3RP	0-200NTU	As above }Suspended solids monitors, a range of c1200 }sensor heads (white light, & infra red)c2000 are available depending on the ranges required. Ultrasonic are available for desludging tanks etc.	c900

A1.8 Data loggers (battery powered) with sensors (all c £3000 - 7500) (graphical output and downloading processors may also be required for convenience, c £1-4000)

Grant (16 channels)	Squirrel 1200 series	needs down loader for continuous use	1000-1300 + sensors
Inst. Freshwat. Ecology (12 channels)	12-bit version	needs micro computer as controller	c2000 + sensors
Solomat (32 channels)	MPM 4000	depth and turbidity sensors available soon	4900

Inst of Hydrology

APPENDIX II List of inland oil spill recovery manufacturers or agents.

Disclaimer: No endorsement of any product is implied by inclusion in this list (or non endorsement by its absence) which is simply an assemblage of product information.

Archaeus Technology Group Ltd
Queen's Building
Kidderpore Avenue
Hampstead
London
NW3 7ST

Tel:(071) 794-5745
Fax:(071) 794-1126

Contact: Anne Jaques

Services: -Oil degradation or clean up using natural biosurfactant compounds.
-Soil washing.

Abzorboil Ltd
11 Simon Evans Close
Cleobury Close
Kidderminster
DY4 8AX

Tel:(0299) 270-179
Fax:(0299) 270-662

Contact: Ralph Walker (Partner)

Services: -Emergency response kits.
-Inflatable booms/mini booms.
-Absorbent pillows etc.
-Rope skimmers.
-3M range of sorbent products including sorbent booms.
-Fastank temporary storage facilities.
-Troilboom river boom systems.
-Oil spill clean-up services.

Euro-matic Ltd
Sinclair House
The Avenue
Ealing
London
W13 8NT

Tel:(071) 991-2211
Fax:(071) 997-5074

Contact: Adrian Wilkes

Services: -SOSOL range of sorbent booms

Fast Engineering Ltd.
Old Mill Industrial Estate
Antrim
Northern Ireland
BT41 4QE

Tel:(08494) 28686
Fax:(08494) 29929

Services: -'Fastank' temporary storage facilities.

Furmanite Engineering Ltd
Furman House
Shap Road
Kendal
Cumbria
LA9 6RU

Tel:(0539) 729-009
Fax:(0732) 740-295

Contact: Mr. W. Bigland (Product
sales administrator)

Services: -Emergency response kits.
 -'Hoyle' of booms.
 -'Slickskim' skimmers.
 -'Vikoma' products including skimmers.
 -'Conwed' sorbent products including booms.

O.M.I. Ltd
Unit G
22 Morley Road
Tonbridge
Kent
TN9 1RA

Tel:(0732) 352-125
Fax:(0732) 352-273

Contact: Mr. R. Stagg (Sales Co-
ordinator)

Services: -Booms and sweeps.
 -Rope skimmers.
 -Disc skimmers.
 -Sorbents.
 -Dispersant systems.
 -Temporary storage facilities.

O.P.D. Ltd
7 Copenhagen Street
Worcester
WR1 2HB

Tel:(0905) 723573
Fax:(0905) 22178

Contact: John Dawes (Director)

Services: -Emergency response kits.
 -Booms (including bubble barriers)
 -Disc skimmers.
 -Sorbents.
 -Pollution training courses.
 -Oil spill clean -up services.

Oil Pollution Environmental
Control Ltd. (OPEC)
1 Nabb Lane
Bristall
Batley
West Yorkshire
WF17 9NG

Tel:(0924) 442-701
Fax:(0924) 471-925

Contact: Peter Ilsley (Director)

Services: -Emergency response kits.
-Booms.
-Rope skimmers.
-Sorbents.
-Temporary storage facilities.

3M (UK) PLC.
Environmental Safety Products
3M House
Bracknell
Berkshire
RG12 1JU

Tel:(0344) 58233

Services: -Range of sorbent materials including booms.

Vikoma International Ltd.
Unit 4a
Blackrock Business Park
Narrowboat Way
Dudley
West Midlands
DY2 0XQ

Tel:(0384) 214944
Fax:(0384) 232160

Contact: Julie Brown (Sales Co-ordinator)

Services: -Pollution response kits.
-Containment booms.
-Disc skimmers.
-Training courses.
-'SPC' range of sorbent products including sorbent booms.

Appendix III

PREPARATION OF FORMAZINE TURBIDITY STANDARD (F.T.U.) for calibration of suspended solids meters.

Solution A

Weigh out 90.9 grams of Analar grade HEXAMINE and dissolve in litre of distilled water.

Solution B

Weigh out 9.09 grams of Analar grade HYDRAZINIUM SULPHATE and dissolve in 1 liter of distilled water.

When required for use mix equal volumes of solution A and B and stand for 24 hours. This time is required for the reaction to complete and total precipitation to take place. The resulting solution is "milky" in colour.

Dilution Formula

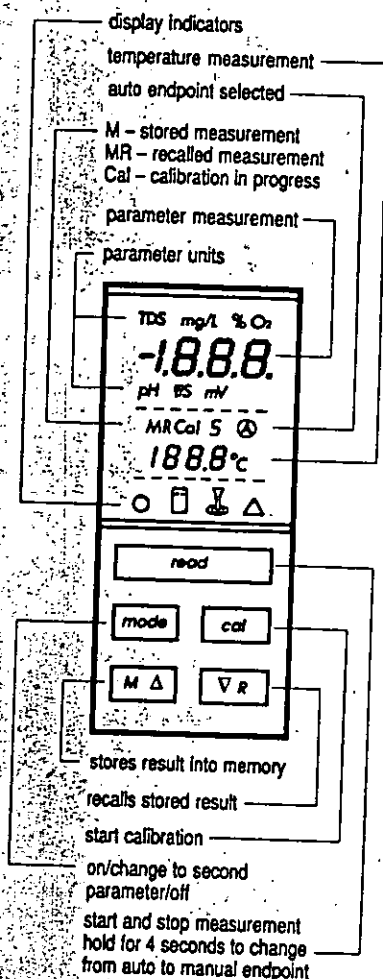
Parts of water required to one part of Formazine Turbidity Standard of 5000 F.T.U.

$$D = 5000$$

where A is the dilution required.

M90 Operating Instructions

The M90 is a portable, microprocessor based, pH, conductivity and dissolved oxygen meter.



Installing the Battery ...

Remove rubber battery door on the rear of the meter.
Fit battery - alkaline type 9V PP3/1604 or equivalent.
Make sure polarity is correct when fitting. The meter must be calibrated after replacing the battery.

Installing a Sensor ...

Locate the pins of the sensor in the meter and push firmly into the meter. The sensor is removed by squeezing down the catch at the rear and pulling the sensor away from the meter.

Making a Measurement ...

pH - remove the sensor wetting cap and slide the vent sleeve to expose the fill hole.

D.O. - remove the sensor wetting cap. Move the sensor in a gentle circular motion when measuring.

Cond - immerse probe to halfway point in solution.

Press **mode**, **read**, **cal** or **M** to turn meter on and start measurement. Place sensor into solution. Automatic endpoint detection freezes the display when plateau is reached; to manually endpoint press **read**. Press **read** again to start new measurement.

Continuous measurement may be selected by pressing and holding **read** for 4 seconds. (In this mode battery consumption is higher and the meter will not automatically switch off when not in use.)

Return to auto endpoint by pressing and holding **read** for 4 seconds.

After use, close the fill hole (pH) and replace the wetting cap (pH and DO).

Calibrating ...

For greater accuracy, calibrate the meter regularly.

1 point

Place the sensor in the calibrating medium:

pH pH 7 buffer 7.00 pH (at 25°C)
Cond Hold in free air 0.00 μS
TDS Hold in free air 0.00 mg/L
DO Zero oxygen solution 0. %O₂
(mg/L O₂ is calibrated in %O₂ mode).

Press **cal** - cal 1 is displayed. After endpointing the display automatically updates to the calibrated value shown, or the temperature compensated value.

If **read** is pressed after Cal 1 update, the meter assumes one point calibration only is required. Samples can now be measured.

2 point

Place the sensor in the second calibration medium:
pH pH 4 or 10 buffer 4.00 or 10.01 pH (at 25°C)
Cond Cond std. A or B 1413 μS or 12.88 mS
TDS Cond std. A or B 706 mg/L or 6.44 g/L
DO Hold in air 10 mm above fresh water 100 %O₂

Press **cal** - cal 2 is displayed. After endpointing the display automatically updates to the calibrated value shown or the temperature compensated value.

Dissolved oxygen only

In practice, cal 2 is required more frequently than cal 1, this is achieved by pressing **cal** twice to advance directly to cal 2.

In mg/L O₂ mode, correction may be made for salinity and barometric pressure. Press **cal** - 100 is displayed. Use ▲ and ▼ to adjust the display according to these tables:

Cond (mS)	Salinity (g/L)	Setting
-	0.0	100
5	2.5	97
11	5.0	95
15	7.5	93
20	10.0	90
24	12.5	88
27	15.0	85
31	17.5	82
34	20.0	81

Barometric Pressure (mm)	Setting	Barometric Pressure (mm)	Setting
600	79	720	95
620	82	740	97
640	84	760	100
660	87	780	103
680	90	800	105
700	92	820	108

e.g. If salinity = 5 g/L setting = 95
if pressure = 740 mm setting = 97
for both parameters, setting will be 95 x 97% = 92.

Using the Memory . . .

5 measurements can be stored in the memory.

Entering a reading into memory

Press **M** when measurement has endpointed.

M 1 (or M 2 - M 5 if readings have already been stored) is displayed indicating that the reading has been saved. Flashing M indicates memory is full.

Recalling memory

Press **R** - the last saved measurement is displayed. Press **R** again to recall the previously saved measurement. MR 1 to MR 5 indicates which saved measurement is being displayed.

Clearing last memory

In memory recall mode (MR) press **M** to clear the measurement being displayed. Only the last entered measurement can be cleared, i.e. if 4 measurements are saved, the M 2 cannot be cleared without first clearing M 4 and M 3.

Clearing all memory

Press **R** until M C is displayed, then press **M**. All memory will be cleared.

Changing Mode . . .

Press **mode** to enter the second function of the sensor, i.e. pH to mV, conductivity to TDS, %O₂ to mg/L O₂.

Press **mode** again to turn the meter off.

Display Codes/Problem Solving . . .

Using the Test Plug

The test plug is provided to test the meter.

Replace the sensor with the test plug and press **read**. The display should read:
7.00 pH \pm 0.5, 25°C \pm 2

E1 - measurement out of range: check that sensor tip is immersed in solution and the wetting cap is removed (if applicable)

E2 - cal 1 out of range | check correct calibration

E3 - cal 2 out of range | medium is used.

Condition/renew sensor

E4 - sensor disconnected



low battery voltage



low electrode slope: condition/renew sensor (pH only)



Default calibration values in memory. Sensor not calibrated (2 point), or battery replaced since last calibration



manual endpoint selected (continuous measurement)



auto endpoint selected

keypad not responding - replace battery and recalibrate.

Operating Hints . . .

1. Use distilled water when transferring from one solution to another.
2. Response time is a function of the sensor and the solution. If the solutions are at different temperatures (or ionic strength - pH only) allow more time for the sensor to respond.
3. Avoid handling the sensor tip.
4. Make sure no large air bubbles are trapped under the sensor when making measurements.
5. Do not use calibration standards after the expiration date.
6. Wetting caps should contain:
pH - pH 7 buffer; DO - distilled water.
7. For greatest accuracy calibrants and samples should be at the same temperature.
8. pH - keep the electrode filled with the appropriate fill solution to prevent reading drift.
9. Conductivity - the sensor shield and probe should be kept clean. Make sure no air bubbles are in the cell chamber during measurement.
10. Dissolved oxygen - the sensor can be removed for several hours as a rechargeable battery in the sensor will maintain polarization. For longer periods the sensor should remain connected to the meter to maintain polarization and recharge the sensor battery.

Reordering Information . . .

Item	Cat.
Meter only	473617
pH sensor	473619
DO sensor	473620
Conductivity/TDS sensor	473621
Hard carrying case	473622
1413 μ S conductivity standard (A), 500 mL	473623
12.88 mS conductivity standard (B), 500 mL	473624
Zero oxygen solution, 500 mL	473625
DO membrane replacement kit	473626
pH 7 buffer sachet (pack of 30)	473650
pH 4 buffer sachet (pack of 30)	473651
pH 10 buffer sachet (pack of 30)	473652
pH multipack, pH 4, 7, 10, (pack of 30 assorted)	473676
pH electrode fill solution, 3 x 5 mL	473654
DO electrolyte, 3 x 5 mL	474594
Buffer solution pH 4.00, 2 x 500 mL (red)	478540
Buffer solution pH 7.00, 2 x 500 mL (yellow)	478570
Buffer solution pH 10.01, 2 x 500 mL (blue)	478510
Replaceable ceramic junctions (pH), pack of 3	477269

Meter Specification . . .

Temperature compensation:	
pH	0 - 100°C
Conductivity/TDS	0 - 50°C
Oxygen	0 - 40°C
Range	
Temp	-0.5°C - 100°C
pH	0 - 14 pH
mV	0 - \pm 1000 mV
Cond	0.00 - 19.99 μ S
	20.00 μ S - 199.9 μ S
	200 - 1999 μ S
	2.00 - 19.99 mS
TDS	0.00 - 10.00 mg/L
	10.0 - 100.0 mg/L
	100 - 1000 mg/L
	1.00 - 10.00 g/L
DO	0 - 200% O ₂
	0 - 20.0 mg/L
Resolution	
	0.1°C
	0.01 pH
	1 mV
	0.01 μ S
	0.1 μ S
	1 μ S
	0.01 mS
	0.01 mg/L
	0.1 mg/L
	1 mg/L
	0.01 g/L
	1%
	0.1 mg/L

Auto switch off: if not operated for 10 minutes after endpoint.

Memory: up to 5 measurements can be stored.

Ciba Corning Diagnostics Limited
Colchester Road
Halstead, Essex, CO9 2DX
England
Tel: 0787 474742

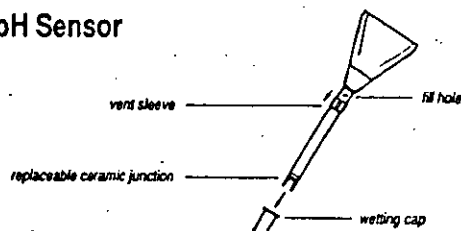
Coming Incorporated
Science Products Division
Coming, New York 14831
USA
Tel: 1-607-737-1667

473655 Rev. A, 3/89

Sensor Information

for pH, DO and Conductivity Sensors

• pH Sensor



For optimum performance:

1. Before use remove wetting cap from tip of sensor, and slide the vent sleeve to expose the fill hole.
2. Make sure that the fill solution is not more than 25 mm (1 inch) below the fill hole. Add KCl solution if necessary.
3. Gently tap the sensor to remove any air bubbles at the ceramic junction.
4. Condition the new sensor by soaking in pH 7 buffer for a minimum of 2 hours.
5. Calibrate and measure samples as described in the M90 instructions.
6. After use, check the level of fill solution, reposition the vent sleeve to cover the fill hole, and replace the wetting cap containing pH 7 buffer (if the sensor will not be used again for more than 2 days, we recommend using saturated KCl in the wetting cap).

Precautions and Limitations:

1. **Do not** wipe the sensor tip - blot dry with a lint-free tissue.
2. **Do not** use KCl saturated with AgCl as this may damage the reference element.
3. **Do not** leave the sensor in organic solvents, strong basic solutions, concentrated fluoride solutions, or hydrofluoric acid for extended periods. Measurements made in these solutions should be taken quickly and the sensor rinsed immediately with distilled water. After rinsing, soak in pH 7 buffer for 2 hours.
4. **Do not** measure solutions that exceed a temperature range of 0 - 100°C.

Maintenance and Troubleshooting:

Prolonged use and ageing may reduce performance i.e. slow response, low slope values, continuous drift or erratic readings. These may be caused by:

Air in junction - remove air bubbles by gentle tapping.

Excess KCl crystals - KCl crystals may build up and settle on the sensor tip, or the KCl may become discolored. Remove the old fill solution and use warm distilled water to dissolve the crystals. Remove water and refill using fresh KCl solution.

Blocked junction - KCl crystals can block the junction. To test for this, blot the tip dry and air dry for one hour. If no KCl crystals appear at the tip of the

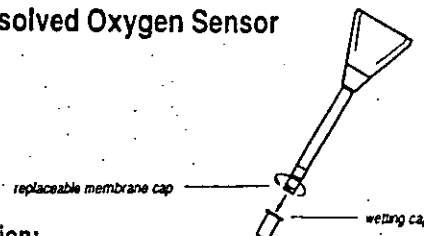
sensor the junction is blocked. Remove the ceramic junction using tweezers, and insert new junction (Cat. 477269). Tap gently to remove any air bubbles.

Contaminated pH bulb - i.e. protein/oil contamination.

Protein - soak the sensor in 10% pepsin solution adjusted to pH 2 with HCl for 30 minutes. Rinse with distilled water and soak in pH 7 buffer for 2 hours.

Oil - wash sensor tip with 50% water-acetone solution. **Do not** soak the sensor in acetone solution as this may cause the seals to deteriorate. Rinse with distilled water and soak in pH 7 buffer for 2 hours.

• Dissolved Oxygen Sensor



Installation:

The sensor is shipped dry and must be filled before use. Unscrew the membrane cap from the sensor and fill using DO electrolyte (Cat. 474594). Gently screw cap onto probe allowing surplus electrolyte to run out. Fit sensor to the meter and allow up to 30 minutes for polarization. Calibrate as described in the M90 instructions.

For optimum performance:

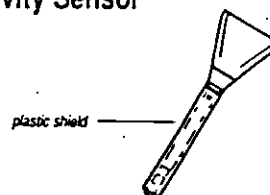
1. Before use remove wetting cap from tip of sensor.
2. The sensor can be removed for several hours as a rechargeable battery in the sensor will maintain polarization. For longer periods the sensor should remain connected to the meter to maintain polarization and recharge the sensor battery.
3. When making measurements the sample should be stirred at a constant speed i.e. approximately 20 cm/second (8 inches/second).
4. Allow sufficient time for the sensor to stabilize when measuring samples of different temperatures - in some cases this can be several minutes. Make sure the sensor is immersed to a depth of at least 40 mm (1 1/2 inches) to cover the temperature sensing element.
5. After use replace wetting cap containing distilled water to prevent electrolyte from drying out.

Maintenance and Troubleshooting:

If the sensor will not calibrate, or becomes sluggish or erratic carry out the following:

1. Remove the membrane cap.
2. Clean the silver and gold anode and cathode using pO_2 electrode cleaning compound (Cat. 477656) and distilled water. Rinse with DO electrolyte (Cat. 474594).
3. Check the membrane for damage and replace with new cap (Cat. 473626) as necessary.
4. Refit cap as described in installation section.

• Conductivity Sensor



For optimum performance:

1. Make sure the clear plastic shield is in place when measuring.
2. When measuring make sure the solution is above the cell chamber rings and below the vent hole.
3. To prevent carryover from high to low conductivity solutions rinse with distilled water between measurements.
4. Make sure the cell chamber is bubble free when measuring. To reduce air bubbles, immerse probe in the solution at an angle and then raise to a vertical position.
5. Clean the probe and shield with distilled water after use.

General Troubleshooting for all Sensors:

1. To verify meter is working check using the test plug.
2. If the sensor connector becomes damaged or wet the display may read E4 when a sensor is connected.
3. If the temperature sensing element becomes damaged the temperature display may read E1 when a sensor is connected.

Ordering Information:

Item	Cat.
pH sensor	473619
pH electrode fill solution, 3 x 5 mL	473654
pH 7 buffer sachet (pack of 30)	473650
pH 4 buffer sachet (pack of 30)	473651
pH 10 buffer sachet (pack of 30)	473652
pH multipack, pH 4, 7 and 10 (pack of 30 assorted sachets)	473676
Buffer solution pH 4.00, 2 x 500 mL (red)	478540
Buffer solution pH 7.00, 2 x 500 mL (yellow)	478570
Buffer solution pH 10.01, 2 x 500 mL (blue)	478510
Buffer rainbow pack, pH 4.00, 7.00 and 10.01 (2 x 500 mL of each)	478574
Replaceable ceramic junctions (pH), pack of 3	477269
DO sensor	473620
DO electrolyte, 3 x 5 mL	474594
Zero oxygen solution, 500 mL	473625
DO membrane replacement kit, pack of 2	473626
pO ₂ electrode cleaning compound	477656
Conductivity/TDS sensor	473621
1413 µS conductivity standard, 500 mL	473623
12.88 mS conductivity standard, 500 mL	473624
Rinse solution sachet (pack of 30)	473653

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Corning Incorporated
Science Products Division
Corning, New York 14831
USA
Tel: 1-607-737-1667

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reagent additions should be of sufficient volume to allow the bottle stoppers to be replaced without trapping air bubbles.

The practice of determining the volume of each sample bottle and titrating its whole contents is time-consuming, and complicates the calculations, but minimizes the loss of iodine by volatilization during transfer and titration (see also below, p. 27). The practice of grinding stoppers obliquely to make it easier to avoid trapping bubbles is, with care, unnecessary.

For use in the field, two 1-ml pipettes graduated in 0.1 ml are required. They should be filled using a rubber bulb or in another way that does not involve suction with the mouth. A variety of pre-set dispensers can also be used.

For titration, a burette is required of capacity appropriate to the chosen titrant strength and volume titrated. Thus, for 0.0125 N thiosulphate solution and 50 ml aliquot, the appropriate capacity is 5 or 10 ml. An interconnected reservoir of titrant is desirable, and a form of piston burette (e.g. Metrohm types E274, E485; Jencons free-piston burette) is recommended for precise work.

Reagents

Various modifications to Winkler's original reagents have been proposed. The highly concentrated reagents (a) and (b) given below were introduced by Pomeroy & Kirschmann (1945).

(a) Manganous sulphate solution

Dissolve 240 g of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in water and dilute to 500 ml.

(b) Winkler's reagent

Dissolve 200 g of sodium hydroxide in 280 ml distilled water. Add 450 g of sodium iodide, cool, and dilute to 500 ml.

(c) 0.1 N sodium thiosulphate

Dissolve 24.82 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and make up to 1 litre.

(d) Starch solution

Bring 100 ml of distilled water to boil in a beaker. Add, with shaking, a slurry of potato starch (1 g shaken in about 10 ml of water in a test tube). Filter, using a large fluted paper; store in a refrigerator. Alternatively, a solution of the readily soluble sodium starch glycolate can be used, or a small quantity of solid 'thiodene'.

(e) Sulphuric acid, 50% v/v solution.

II

DISSOLVED GASES OF BIOLOGICAL SIGNIFICANCE

1. DISSOLVED OXYGEN

Two main types of determination are in common use. The older titration procedure is more time-consuming but can afford high precision and accuracy. It also enables samples to be stored. The electrode-probe method is rapid, can be used *in situ* (so dispensing with samples) as well as in the laboratory, and is relatively free from interferences, but high accuracy (better than about $\pm 3\%$) is difficult to maintain.

A. BY TITRATION (Winkler 1888)

Principle

A white precipitate of manganous hydroxide is generated in the sample which absorbs any oxygen to form a brown manganic oxide of uncertain composition. After acidification, Mn^{4+} reacts with iodide to liberate iodine, in an amount equivalent to that of the original oxygen. The iodine is determined by titration with thiosulphate.

Apparatus

Samples are collected in glass stoppered bottles, most conveniently of 110–130 ml capacity. With these one can remove 50 ml for titration, leaving enough for a repeat titration if necessary. If preferred, bottles holding about 30 ml can be used perfectly satisfactorily, with a corresponding reduction of the volumes of reagents and removal of 10 ml for titration. It should be noted, however, that the smaller volume requires greater care not only in the titration but also in the handling of the samples so as to avoid significant changes by contact with the air. Also, the

(f) 0.100 N potassium iodate

Dissolve 3.567 g of KIO_3 in distilled water, and make up to 1 litre in a graduated flask.

(g) Potassium iodide crystals.

(h) 2 N sulphuric acid.

(a) Standardization of thiosulphate solution

Dilute the thiosulphate solution (c) to approximately 0.0125 N (N/80), and put it into the burette. Dilute standard iodate solution (f) to exactly 0.0100 N, by removing 25 ml and making up to 250 ml in a graduated flask. Into a 400-ml conical flask put:

- approx. 2 g (i.e. excess) of solid potassium iodide, 150 ml of distilled water,
- 5 ml of 2N sulphuric acid (h),
- a few drops of starch indicator (d).

If any blue colour develops, discharge it with a drop of thiosulphate solution. Add 10 ml of iodate. Run in thiosulphate from the burette with constant shaking until the blue colour is just discharged, completing the titration at the end of 2 min. Calculate the normality of the thiosulphate solution; 0.0125 N (N/80) is chosen for the approximate strength of this solution because, when titrating a treated sample of 100 ml, each ml of a *precisely* 0.0125 N solution is equivalent to 1 mg of oxygen per litre. Sometimes, for convenience, other sample volumes and titrant strengths may be preferred.

As thiosulphate standards deteriorate with time, more rapidly if diluted, the 0.0125 N solution should be checked afresh every day of use.

(b) The determination of the dissolved oxygen content of a sample

In the field

Carefully fill one of the stoppered bottles, arranging for the sample to flow into the bottle through a tube from the water-sampler reaching to the bottom. Allow it to overflow, flushing the bottle with about twice its volume of sample, and avoid the entrainment of air bubbles. The bottle is disconnected and stoppered, care being taken not to trap an air bubble.

Within a few minutes of filling it remove the oxygen-bottle stopper, and with pipettes introduce below the surface 0.5 ml of manganous sulphate (a) and 0.5 ml of Winkler's reagent (b) for every 100 ml of bottle

volume. Replace the stopper firmly, again taking care to avoid trapping air, and shake well. (On replacing the stopper a small amount of water equal in volume to the added reagents is expelled.) A precipitate of manganous hydroxide is formed, some of which is oxidized to a manganic oxide-hydroxide by the oxygen present in the sample.

On returning to the laboratory

Allow the precipitate to settle; if slow, a second shaking may be helpful. At this stage the sample can be stored for several days, preferably submerged in water. Introduce 1.0 ml of sulphuric acid (c) per 100 ml of bottle volume, and replace the stopper quickly and firmly, avoiding loss of precipitate or the trapping of air. Shake well. The precipitate dissolves and the manganic ions in acid solution oxidize iodide to tri-iodide (I_3^-) and free iodine. A rough estimate of the amount of oxygen present in the sample can be made by noting the depth of colour of the iodine at this stage.

Transfer with a pipette 10, 50 or 100 ml to a conical flask. Titrate with 0.0125 N thiosulphate until only a faint yellow colour remains; add a few drops of starch indicator (d) and take the end-point as in the standardization. The titration should be made as speedily as accuracy permits to reduce iodine loss by volatilization. This error is minimized by the high concentration of iodide (and hence tri-iodide) from the Winkler reagent (b), but possible further precautions include (i) transfer of sample by a syringe-based dispenser (e.g. Jencons' 'Zippette', 30 ml size), (ii) addition of most of the titrant required to the flask before the sample, (iii) titration of sample within the sampling bottle, using a micro-burette with magnetic stirring (cf. p. 52), and (iv) adding the sample to excess thiosulphate and back-titrating with iodate.

The end point can be found more accurately, and objectively, by use of a simple amperometric circuit (that of Fig. 4a with the 1-volt potential source removed) based on a platinum-calomel electrode pair. This is most conveniently used in the form of a dual (combination) electrode, such as the types EA216, EA217 and EA234 of Metrohm, or 1143 of Electronic Instruments Ltd. If the circuit is completed through some external conductor or resistor, a current will flow so long as free iodine is present before the end-point, declining as the latter is approached. After the end-point, a small, constant, residual current will exist. Unwanted 'drifts' can often be eliminated by a preliminary cleaning of the Pt electrode tip (e.g. by immersion in concentrated nitric acid for 20 min). The changes in current can be detected with a series microammeter (e.g. 0–25 μA), or with a pH meter (functioning as a millivoltmeter) connected across a high resistor (e.g. 100 k Ω) that is in series with the electrode. Since the change in current (or

derived potential) is linear with titrant volume to quite near the end-point, the latter can be located from a few readings (cf. Fig. 4c; p. 105). Details of possible procedures, including also back-titrations with iodate after over-neutralization with thiosulphate, and adaptations for small volumes (e.g. 2 ml), are described by Talling (1973). The iodine end-point can also be located electrochemically with the simple and robust tungsten-electrode system devised by Potter (see Potter & White 1957) and marketed by Electronic Instruments Ltd; it is used in conjunction with a pH meter and preferably in a back-titration.

Accurate determination of the end-point is also possible by photometric titration using the changing absorption of ultra-violet radiation. A procedure is described in detail by Bryan, Riley & Williams (1976).

Calculation

One molecule of oxygen is equivalent to two molecules of iodine produced at the end of the reaction in the bottle. Since in the titration $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$, it follows that 1 ml of 0.0125 N thiosulphate is equivalent to 0.1 mg O_2 (0.070 ml at 0 °C and 760 mm Hg pressure). More generally, if v = volume of thiosulphate of normality n (determined by standardization) used in the titration, and V = volume of sample titrated (both volumes in ml), then

$$\begin{aligned} \text{oxygen concentration in sample} &= (8000 \, n/V) \, v \quad (\text{in mg l}^{-1}) \\ &= v \text{ when } n \text{ is } 0.0125 \text{ and } V \text{ is } 100 \text{ ml} \\ &= (250 \times 10^3 \, n/V) \, v \quad (\text{in } \mu\text{mol l}^{-1}) \end{aligned}$$

Strictly, a correction, usually neglected, is necessary for the effect of oxygen introduced by the Winkler reagents (a) and (b), less than in the 1% of sample water displaced by the addition of these reagents. It can therefore vary from a negative to a positive quantity as the oxygen concentration of the sample increases. For anoxic samples it is approx. $-0.1 \text{ mg } O_2 \text{ l}^{-1}$, and for air-saturated samples $< +0.1 \text{ mg } O_2 \text{ l}^{-1}$.

Note

Estimation of the liberated I_2 may be made more rapidly, though less accurately, by spectrophotometry. Absorbance of a diluted aliquot can be measured at or near 430 nm in cells of 1 cm pathlength, and calibrated against quantities found by titration. This and other modifications are described by various authors (e.g. Duval et al. 1974). The method is unsuitable for waters with much particulate material, which interferes by its optical and I_2 -absorbing properties.

(c) Calculation of percentage saturation

TABLE 2

Solubility of oxygen in distilled water in equilibrium with air at normal pressure (760 mm Hg) and 100% relative humidity (from Montgomery, Thom & Cockburn 1964; closely similar values are given by Carpenter 1966 and Murray & Riley 1969)

Temperature of sample °C	C_s Solubility mg l ⁻¹ $\mu\text{mol l}^{-1}$	Temperature of sample °C	C_s Solubility mg l ⁻¹ $\mu\text{mol l}^{-1}$
0	14.63	18	9.46
1	14.23	19	9.27
2	13.84	20	9.08
3	13.46	21	8.91
4	13.11	22	8.74
5	12.77	23	8.57
6	12.45	24	8.42
7	12.13	25	8.26
8	11.84	26	8.12
9	11.55	27	7.97
10	11.28	28	7.84
11	11.02	29	7.70
12	10.77	30	7.57
13	10.53	31	7.45
14	10.29	32	7.33
15	10.07	33	7.21
16	9.86	34	7.09
17	9.65	35	6.98

The saturation concentration (C_s) at the temperature at which the sample was taken may be found from Table 2 by interpolation. Then if the actual concentration of oxygen in the sample is found by analysis to be C , the percentage saturation is given by $100 \times C/C_s$.

The value of C_s also varies with pressure. If the sample was not taken at sea level, the value of C_s from Table 2 should be corrected for altitude by division by the appropriate correction factor extracted from Table 3. A further correction for salinity is required only in exceptionally saline freshwaters.

TABLE 3

Correction factors for altitude (from Mortimer 1956)

Altitude (m)	Correction factor	Altitude (m)	Correction factor
0	1.00	1300	1.17
100	1.01	1400	1.19
200	1.03	1500	1.20
300	1.04	1600	1.22
400	1.05	1700	1.24
500	1.06	1800	1.25
600	1.08	1900	1.26
700	1.09	2000	1.28
800	1.11	2100	1.30
900	1.12	2200	1.31
1000	1.13	2300	1.33
1100	1.15	2400	1.34
1200	1.16	2500	1.36

(d) Dissolved oxygen in waters rich in organic matter

Some waters, owing for example to pollution by sewage or trade wastes, contain sufficient organic matter or other reducing agents (e.g. NO_3^- , Fe^{2+}) to interfere with the essential reactions of the Winkler method. For these a number of special techniques have been devised, for discussion of which the standard textbooks (e.g. American Public Health Association 1976) should be consulted. Interference by nitrite can be eliminated by incorporating a quantity of sodium azide (10 g l^{-1}) in the alkaline iodide reagent (b). A simple modification suitable for waters rich in organic matter is the bromosalicylic method of Alsterberg (1926). In this the organic matter is first oxidized by the addition of a bromine solution in the field, after which the stoppered sample is kept under water for 24 h. Sodium salicylate is then added to react with the excess bromine and the ordinary Winkler procedure is followed.

Variants of the procedure, and sources of error, are considered by Rebsdorf (1966).

Reagents in addition to those, (a) to (h), used for the unmodified Winkler method

(j) Bromine solution (toxic vapour: handle with care, and do not dispense with a mouth pipette!)

Potassium bromate (KBrO_3) 3 g
Sodium bromide (NaBr) 20 g
Hydrochloric acid (conc.) 25 ml
Distilled water to 100 ml

(k) Sodium salicylate, 10% w/v solution

Dissolve 10 g of sodium salicylate in 100 ml of distilled water.
Discard when strongly discoloured.

Procedure

Take the sample, observing the same precautions as for the ordinary Winkler method. To each bottle add (e.g. by bulb-operated pipette) 0.5 ml of bromine solution (j) per 100 ml of sample, and re-stopper quickly. On return to the laboratory immerse the sample bottles in water, and keep them in the dark 24 h. Then add 0.5 ml of salicylate solution (k) for each 0.5 ml of (j) previously added; shake, and leave 15 min. Now proceed as in the ordinary Winkler method by adding the appropriate amounts of reagents (a) and (b) and continuing as described above. Calculations are not affected by the modification, except that displacement of sample (with oxygen) by reagents is increased from 1 to 2%.

(e) Dissolved oxygen in waters of high alkalinity

Principle

In such waters, rich in bicarbonate plus carbonate, difficulties are encountered with the Winkler method, due to effervescent liberation of CO_2 at the acidification stage. Iodine-containing solution may then be lost from the bottle, and accuracy drops rapidly above an alkalinity of about 50 meq l^{-1} .

With the 'Miller method' (see Walker et al. 1970, Ellis & Kanamori 1973) there is no acidification, and the dissolved oxygen is titrated directly with ferrous ions in alkaline solution.

Reagents

- (a) Alkaline tartrate solution
Dissolve 15 g of sodium hydroxide and 10 g of potassium sodium tartrate in 50 ml distilled water.
- (b) Ferrous titrant solution (approx. 0.1 N)
Dissolve 10 g of ferrous ammonium sulphate hexahydrate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in 250 ml of distilled water acidified with 0.5 ml of conc. sulphuric acid. Standardize against dichromate (see p. 106). This concentration of ferrous salt is suitable for a 2.5-ml burette and 125 ml sample volume. For a 0.5-ml burette it should be increased 3 to 5 times.
- (c) Redox indicator (if used)
Dissolve 0.1 g of phenosafranine in 100 ml of distilled water.

Procedure

As applied by us, the sample is collected in a stoppered bottle, as before, and rendered strongly alkaline (pH c. 10.3) by the addition of 0.3 to 0.6 ml (per 100 ml sample) of alkaline tartrate reagent (a). Using magnetic stirring, titration is carried out *in the sample bottle* with a solution of ferrous ammonium sulphate (reagent b) from a micro-syringe (0.5 to 2.5 ml) or piston burette (e.g. the 'Agla' of Wellcome Reagents Ltd.). The burette tip passes through a suitably shaped stopper (with fine vent hole) which prevents entry of atmospheric oxygen during the titration, when some sample is displaced by titrant. The end-point is found either by the colour change of a suitable redox indicator (e.g. phenosafranine, reagent c) or amperometrically using a combination platinum-calomel electrode and potential source. The electrode system is inserted into the sample bottle in parallel with the burette tip, through the stopper, and with the Pt electrode maintained at -0.3 V by a potential source (for circuit and components, see Fig. 4a and p. 102). Readings of current (or derived potential) are taken on a suitable meter (e.g. type TM9B of Levell Electronics), some 20 seconds after each addition of titrant, and the end-point (v , in ml) located from the final discontinuity in a plot against titrant volume. The oxygen concentration x (as mg l^{-1}) is then calculated as:

$$x = \frac{(n \cdot f \cdot 8000) v}{V}$$

where V = volume of sample titrated (ml)

n = normality of titrant

f = a factor which varies with pH of the titrated sample, approaching 1 at pH 12.2-12.6 (Ellis & Kanamori 1973). It

was determined as 0.92 (± 0.02) for the conditions given above (Talling & Kenley, unpublished).

Corrections may be applied (see Ellis & Kanamori 1973) for oxygen added, or sample volume displaced, by reagents; they will not exceed 2% with the above procedure.

If samples must be stored before titration, a preservative may be incorporated with the first alkaline tartrate reagent, which is added to samples soon after collection.

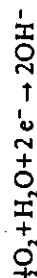
The following method can also be used for waters of high alkalinity.

B. DETERMINATION BY AN OXYGEN ELECTRODE PROBE

The determination of dissolved oxygen in natural waters is most conveniently carried out by means of an oxygen - temperature probe. Various forms are commercially available (e.g. Lakes Instruments, Electronic Instruments Ltd., Uniprobe Instruments, Delta Scientific, Partech (all Mackereth-type); Yellow Springs Instrument Co., Sinac Instrumentation, Beckman, Hach, Philips). Many can be used for measurements *in situ* as well as in the laboratory. Those based on the Clarke (Pt-Ag) electrode system require an external polarizing potential, generate a relatively small current, and require at least daily standardization. The following account is based upon the galvanic cell devised and described by Mackereth (1964), which requires no external polarizing potential, generates a relatively large current, and is stable over considerable periods. The housing incorporates a thermistor, freely exposed to the medium, by which temperature can be measured. Other modifications exist (e.g. Flynn et al. 1967, Harrison & Melbourne 1970).

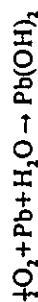
This device consists of a galvanic cell protected from the external environment by a membrane which is permeable to gases but to little else. The cell consists of a perforated cylindrical silver electrode inside which is a large porous annular lead electrode. The two electrodes, together with a thermistor, are mounted on a plastic body, and the cell is isolated from the external medium by a polyethylene membrane covering the silver electrode. The electrolyte in the cell is saturated aqueous potassium hydrogen carbonate, which may be incorporated in an agar gel.

The oxygen present at the silver electrode reacts with electrons to produce hydroxyl ions as follows:



At the lead electrode loss of electrons has produced lead ions thus: $\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$; the lead ions combine with the hydroxyl ions to

precipitate lead hydroxide on the lead electrode. The overall cell process is then:



When the silver and lead electrodes are connected through the external circuit, which includes a current-measuring device (resistance <200 ohms), electrons pass from the lead electrode to the silver electrode. The rate of the reaction is controlled by the supply of oxygen to the silver electrode. Unwanted secondary (diffusive) limitations must be avoided by sufficient movement of the medium at the membrane surface. Under these conditions, the magnitude of the electric current in the external circuit is related to the oxygen concentration and temperature of the medium. The temperature coefficient is approximately +6% per °C.

When not in use, the probe should be kept in a deoxygenated solution. This can be produced by dissolving a little solid sodium sulphite in water, or by allowing the probe itself to consume the dissolved oxygen of water within a small, sealed space. The most common cause of malfunction is rupture of the thin membrane which must then be replaced, with electrolyte if necessary.

Operation

For measurements *in situ*, it is sufficient to suspend the cell in standing water, by an electrical cable of suitable length, and raise and lower it to produce a water flow over the polyethylene membrane. The stirring should be sufficient for the reading to be unresponsive to increased agitation. When the microammeter reading is steady, the current flowing is noted and the thermistor reading is taken. The oxygen electrode reading is then divided by a sensitivity factor, equal to current *i*/oxygen concentration $[\text{O}_2]$ (e.g. in μA per mg l^{-1}) at the temperature (thermistor reading) involved, whose variation with temperature is known from independent calibration, to obtain the oxygen concentration (e.g. in mg l^{-1}).

As the sensitivity factor is independent of oxygen concentration, it may be found, for a given temperature, from readings at any suitable and known concentration. The latter may be determined by the Winkler analysis, or by preparing a well-aerated and hence air-saturated solution whose concentration is found, after correction for atmospheric pressure, from Table 2. By repeating the procedure at a series of temperatures within the range of operation, a calibration graph relating sensitivity factor to temperature can be constructed. It should be periodically checked, and recalibrations made when necessary. Alternatively a simple equation can be fitted to the data and used for later calculations. One good approximation

(for another see American Public Health Association 1976, p. 451) is

$$\log F = a - b/T$$

where F is the sensitivity factor, T the absolute temperature in K ($^{\circ}\text{C} + 273$), and a and b are constants represented by the intercept and slope of a plot of $\log F$ against $1/T$. Then, since $F = i/[\text{O}_2]$, $[\text{O}_2] = i \text{ antilog } [(b/T) - a]$.

The cell and read-out can be modified to give a direct reading of percentage oxygen saturation or concentration, by incorporation of a thermistor-based compensation circuit (cf. Briggs & Viney 1964), or by a scaling potentiometer which is set according to the temperature reading.

The read-out may be on a microammeter, with a range of 0–500 μA for the original Mackereth electrode but less for many other forms. Alternatively, a millivoltmeter may be used connected across a load resistor of about 100 ohms; small, battery-operated digital panel meters reading to 0.1 mV have proved useful for field-work.

For laboratory measurements in small vessels, various smaller probes are available. Some incorporate a stirring device, which may otherwise be provided by a magnetic stirrer.

2. FREE AND TOTAL CARBON DIOXIDE

Unlike oxygen, the carbon dioxide dissolved in natural waters ($\text{CO}_{2(\text{aq})}$) participates in interconnected equilibria that typically involve much larger quantities of the gas 'bound' in ionic form, as bicarbonate and carbonate ions:

- (i) $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_{2(\text{aq})}$
- (ii) $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$
- (iii) $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$
- (iv) $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$
- (v) $\text{CO}_3^{2-} + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$
- (vi) $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

It is customary to distinguish as 'free carbon dioxide' the concentrations of CO_2 plus H_2CO_3 ; the latter comprises a very small percentage of this sum.

The concentration of free CO_2 present in a water sample that is in gaseous equilibrium with the atmosphere can be calculated as the product of the solubility of pure CO_2 and the fractional content of CO_2 in air (~0.00033). A correction for altitude (pressure) can be made as for dissolved oxygen (table 3, p. 30). At normal pressure, and a fractional content of 0.00033, the concentrations for pure water at 0, 10, 20 and 30 °C are respectively 26, 18, 13 and 9.8 $\mu\text{mol l}^{-1}$.