(K) Electric Conductivity

Set a constant voltage between electrodes and obtained a conductivity by measuring AC current flowing in the solution and indicated it in μs/cm.

(L) Sodium and Potassium

Introduced the top clear part of the sample directly into atomic absorptiometer and measured sodium and potassium.

(M) Manganese, Iron, Copper, Lead, Chromium and Zinc

After adding hydrochloric acid to the sample, introduced the solution into atomic absorptiometer and then measured these.

(N) Ultraviolet Absorption

After filtering the sample by a 0.45 μm bore diameter membrane filter, measured the absorbance at 250 nm wavelength by using absorptive cell of 1 cm light path length.

(O) Fluorescence Intensity

After filtering the sample by a 0.45 μm bore diameter membrane filter, measured the fluorescence intensity of 430 nm wavelength at 330 nm excitation wavelength. Measured value varies depending on the type of fluorometer. The fluorescence intensity is useful as an index for estimation of fulvic acid.

(P) Dissolved Organic Carbon

The same method as used at the WAL.

2) Results and Discussions

Table 1 Jar Test Results of Water Quality

		Aluminum Sulfate Dose (mg/ℓ)	Turbidity (NTU)	pH	DOC
Raw Water (Collection Point)		0	86	8.1	3.8
Coagulated Water	No. 1	10	26	7.9	3.7
	No. 2	20	15	7.7	2.9
	No. 3	30	6.7	7.5	3.4
	No. 4	40	5.5	7.4	5.5
	No. 5	60	3.2	7.3	3.6

In Japan we measured THM formation potential about the coagulated-settled raw water and the jar tested water. The test results are given in Table 2. About the THM formation potential, we compared the water samples taken at Inlet of the Canal and at Addassiyyeh and found out that the potential was approximately 1.5 times higher in the Canal water. From this, it is known that contamination is present somewhere along the Canal and also that, of the THM formed by the influence of bromide ion in the raw water, the proportion of the bromine containing THM is large. As viewed from the amount of organic matter in the water, the THM formation potential is large. This is due to the large amount of brominated THM. About the relation between the bromide ion in raw water and the forming THM potential, Equation (1) as follows is proposed for testing concerning humic acid 5 mg/ℓ solution:

$$[\mathrm{THM\ Br}] = k\,[\mathrm{Br}^-]^{0.86} \quad \cdots\cdots \quad (1)$$

THM Br : Amount of total brominated THM (μ mol/ℓ)
Br^- : Concentration of bromide ion (μ mol/ℓ)
k : Invariables pH 4 : 0.05 pH 7 : 0.13 pH 10 : 0.22

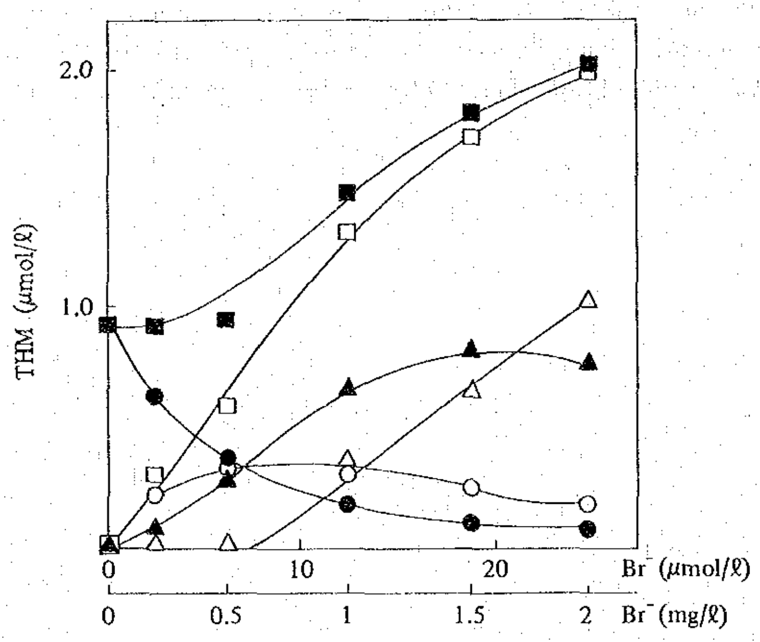
The precursors in raw water can be generally divided into the suspensory precursor and the dissolved precursor. The former is approximately 40 % in view of the fact that about 40 % of the THM formation potential can be reduced by filtration with a 0.45 µm membrane filter. Approximately 30 % of the latter, on the other hand, can be removed by dosing 60 mg/ℓ aluminum sulfate and then by filtration after coagulation and settling, therefore, approximately 60 % in total of the precursors can be removed from raw water by filtration after coagulation and settling.

The THM formation potential of the water measured in Japan, as shown in Table-3, was higher than that showned in Table-2.

The reason is, in our opinion, that the THM formation potential varies extensively depending on the chlorination conditions such as (1) the mass of the precursor in the sample, (2) the pH in chlorination, (3) the temperature in chlorination, (4) the residual chlorine concentration in chlorination, (5) whether the residual chlorine is free or combined, (6) the reaction time with chlorine and (7) the concentration of bromine ion.

Table 2 Test Results of Trihalomethane Formation Potential

	Sample	Rate of Chlorine Dose	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
1	Inlet	10	48	74	102	40	264
2		20	74	112	120	36	342
3	Inlet, after filtration by 0.45 μm filter	5	8	26	70	48	152
4		10	16	40	90	44	190
5	Addassiyyeh	10	8	44	66	48	166
6		20	20	41	78	44	183
7	Addassiyyeh, after filtration by 0.45 μm filter	5	4	10	44	60	118
8		10	4	10	42	54	110
9	Inlet, after coagulation and settling (Alum 60 mg/ℓ)	5	4	18	48	32	102
10		10	10	24	48	20	102
11	Purified Water (Laboratory)	—	0	2	4	6	12



(Chlorine Dose: 10 mg/ℓ at 20°C, Contact Time: 24 hours)

Fig. 1 Amount of Bromine Ion Addition and Amount of THM Formation (pH 7)

Table 3 Water Quality of Raw Water and Tap Water

(mg/ℓ)

Item \ Sample		Raw Water	After filtration 0.45 μm membrane filter	Raw Water	After filtration 0.45 μm membrane filter	Raw Water	After filtration 0.45 μm membrane filter	Tap Water
Place of Sampling		Addassiyyeh	Addassiyyeh	Deir Alla	Deir Alla	Up Stream on Deir Alla	Up Stream on Deir Alla	Hotel Marriot
Date of Sampling		May 28, '85	May 28, '85	May 28, '85	May 28, '85	May 30, '85	May 30, '85	June 1, '85
Tarbidity (JTU)		30	0.5	30	1.0	30	–	0
Color		–	6.0	–	8.0	–	–	1.0
pH Value		8.0	8.2	7.9	8.0	8.0	–	7.4
Alkalinity (as $CaCO_3$)		214	226	211	214	204	–	157
Chloride (Cl^-)		103	103	116	120	137	–	82
Bromide (Br^-)		–	–	–	–	0.8	–	–
Sulfate (SO_4^{--})		85	78	110	104	110	–	37
Nitrate (as N)		4.0	3.5	3.5	3.4	3.4	–	6.1
Ammonia (as N)		0.00	0.00	0.00	0.00	0.00	–	0.00
$KMnO_4$ Consumed		6.2	4.6	10.6	8.1	10.9	–	0.9
Total Hardness (as $CaCO_3$)		270	260	280	290	285	–	185
Total Dry Solid		574	549	682	590	652	–	409
Electric Conductivity (μs/cm)		884	896	969	987	985	–	685
Sodium (Na^+)		83	85	97	97	97	–	75
Potassium (K^+)		4.2	4.1	6.1	6.3	6.8	–	4.3
Manganese		0.02	0.00	0.05	0.00	0.02	–	–
Iron		0.75	0.01	0.93	0.02	0.44	–	–
Copper		0.00	0.00	0.00	0.00	0.00	–	–
Lead		0.00	0.00	0.00	0.00	0.00	–	–
Chromium		0.00	0.00	0.00	0.00	0.00	–	–
Zinc		0.01	0.01	0.01	0.01	0.01	–	–
UV Absorption (250 nm)		0.040	0.042	0.067	0.066	0.072	–	0.017
Fluorecence Intensity		80	88	129	138	133	–	14
Dissolved Organic Carbons		1.5		2.7		3.3	–	–
Torihalomethane Formation Potential (μg/ℓ)	$CHCl_3$	10	5	20	8	20	8	–
	$CHCl_2Br$	22	14	32	28	34	30	–
	$CHClBr_2$	42	36	45	46	48	42	–
	$CHBr_3$	32	26	21	26	22	22	–
	TTHM	106	86	118	108	124	102	–

In Japanese authorized analytical method, chlorination is made under a set of conditions, as follows, in order to obtain a THM formation potential:

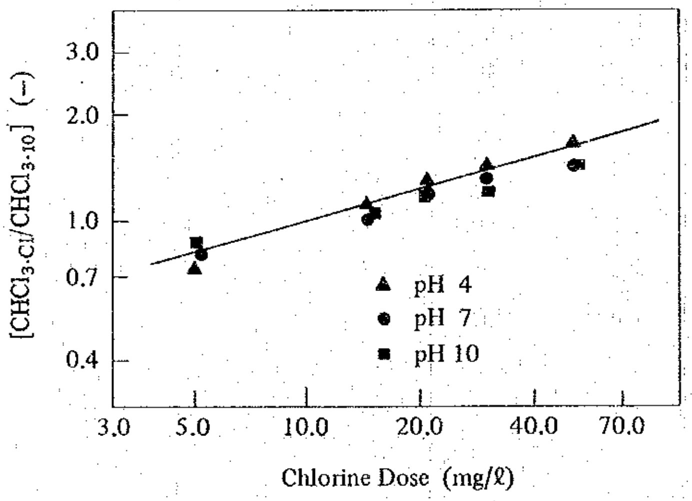
1) The TOC in the sample be no larger than 5 mg/ℓ.
2) The pH be 7.0 ± 0.2.
3) The temperature at the time of chlorination be 20°C.
4) The duration of chlorination be 24 hours.
5) The free residual chlorine thereafter be 1.0 mg/ℓ.

In the THM formation potential test made at the WAL, it became impossible to determine a chlorine dose after obtaining a chlorine consumption in the sample. For this reason, chlorination was made after dosing an excessive amount of sodium hypochlorite in an attempt to secure free chlorine after 24 hours. As the result, an excess amount of free chlorine remained after 24 hours and the pH rose to more or less 9 by the sodium hydroxide included in the sodium hypochlorite solution, according to our assumption.

About the relation between the concentration of free residual chlorine after 24 hours and the THM formation potential, Equation (2) and Fig. 2 are applicable concerning the 5 mg/ℓ humic acid solution. So, the THM formation potential should increase as free chlorine remained in excess.

$$\left[\frac{CHCl_3 \cdot Cl_2}{CHCl_3 \cdot 10}\right] = 0.53\,[Cl_2]^{0.27} \quad \cdots\cdots (2)$$

$CHCl_3 \cdot Cl_2$: Amount of chloroform formation (μg/ℓ) in chlorine dose Cl_2 (mg/ℓ)
$CHCl_3 \cdot 10$: Amount of chloroform formation (μg/ℓ) in 10 mg/ℓ chlorine dose



(Condition: 5 mg/ℓ humic acid, one day reaction time, 20°C. temperature)

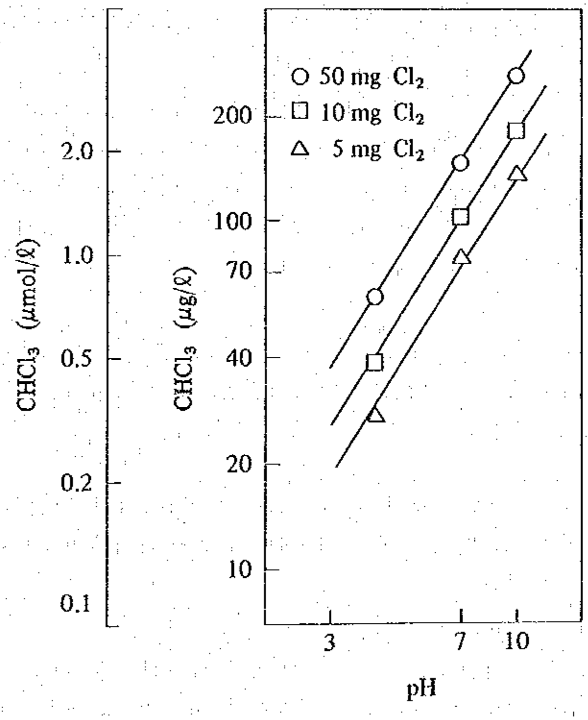
Fig. 2 Relation between Chloroform Formation and Chlorine Dose

Also, the relation between pH and THM formation potential about the 5 mg/ℓ humic acid solution is such as shown in Equation (3) and Fig. 3 below, by which the difference is about two-fold in THM formation potential between pH 7 and pH 9. This is the reason in our opinion for the outcome that the THM formation potential in n-pentane extraction liquid after chlorination which was made at WAL and measured in Japan is higher than the THM formation potential which was both chlorinated and measured in Japan.

$$\left[\frac{\mathrm{CHCl_3 \cdot pH}}{\mathrm{CHCl_3 \cdot 7}}\right] = 0.04\,[\mathrm{pH}]^{1.59} \quad \cdots\cdots\cdots \quad (3)$$

$CHCl_3 \cdot pH$: Amount of Chloroform Formation (μg/ℓ) in reactive pH
$CHCl_3 \cdot 7$: Amount of Chloroform Formation (μg/ℓ) in pH 7

According to the above, we made a review combinedly over the THM formation potential test at the WAL and the quality test results of the water samples in Japan, and we can say that those THM formation potential values shown in Table 2 are correct. Furthermore, we consider from the fact that the water samples taken at Inlet and at Addassiyyeh differ much in quality and that the THM formation potential and the inorganic ion between the upstream and the down stream are of the same rate that the increase of THM formation potential toward the downstream originates in the agricultural waste water flowing into the Canal.



(Condition: 5 mg/ℓ humic acid, one day reaction time, 20°C. temperature)

Fig. 3 Relation between Chloroform Formation and Reactive pH

3. THM Control Simulation Tests for Zay Water Purification Plant

For the purpose of finding appropriate measures to reduce trihalomethane (THM), we conducted simulation tests within the Zay Purification Plant, using all available methods. The sample water used for these tests was the one taken at a point along the East Ghor Canal, about 5 km upstream from Deir Alla.

The simulation test contents are given in Fig. 3-1 through Fig. 3-11.

The amount of sample used for the tests was 500 mℓ per case. Into each beaker we gave the test chemicals and, after coagulation in jar tester (at 140 rpm for one minute and 60 rpm for ten minutes), left the solution for ten minutes. Then, we filtered the supernatant of it by glass fiber filter paper and measured an amount of THM for six to 96 hours.

Excepting the powdered activated carbon (PAC) available at Zay Purification Plant, all the chemicals used were of Japanese production. For chlorination, we used sodium hypochlorite.

The simulation test results are shown in Fig. 3-1 through Fig. 3-11 and also summarized in Table 3-1.

3-1 Comparison of Simulation Tests

(1) Cases No. 1 and No. 2

The tests as Cases No. 1 and No. 2 were made to confirm whether the dosing of $KMnO_4$ would be effective or not in the process of pre-chlorination. As the result, we discovered that there was no reduction in the amount of TTHM formation attained by this kind of treatment; no difference from pre-chlorination alone. Therefore, the use of $KMnO_4$ is ineffective.

(2) Cases No. 3 and No. 5

On these comparative cases, we checked how the TTHM formation would be affected by the use of $KMnO_4$ in combination of powdered activated carbon (PAC) and intermediate chlorination. As the result, we observed that Case No. 3 (189 μg/ℓ) was more effective by 30 – 40 % than Case No. 5 (257 μg/ℓ) in the removal of TTHM. Accordingly, it is known that the use of $KMnO_4$ is effective to some degree.

(3) Cases No. 4 and No. 5

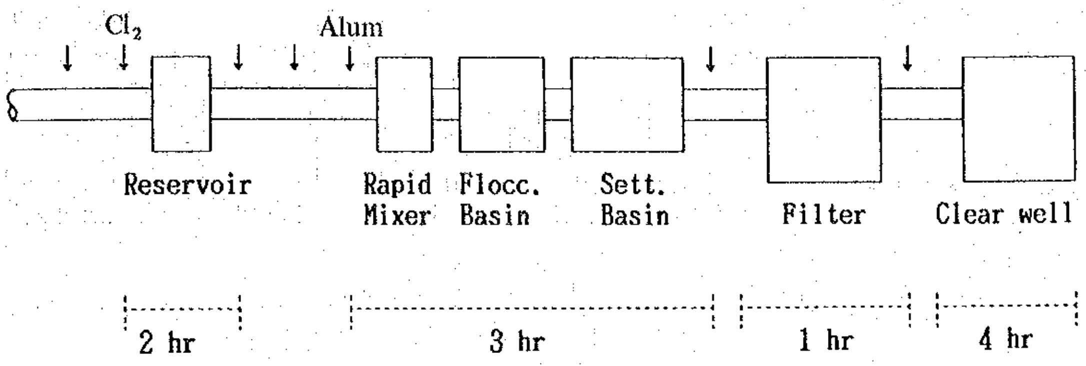
Comparison was made of the two cases of lowering and not lowering the pH for coagulation by the combined use of PAC and intermediate chlorination. As the result, we found it possible to reduce the amount of TTHM formation by more than 50 % in Case 4, much better than in Case 5.

Even when Case No. 4 is compared with Case No. 3, it is noticed that the TTHM formation is reduced from 189 μg/ℓ to 109 μg/ℓ. Therefore, it is known that lowering of pH is an effective means for TTHM reduction.

(4) Cases No. 6 and Nos. 3, 4 and 5

In Case No. 6, the sample was coagulated at a low pH and intermediate chlorinated. The TTHM in Case No. 6 which is 117 μg/ℓ is better than 189 μg/ℓ in Case No. 3 and than 257 μg/ℓ in Case No. 5. Cases No. 4 and No. 6 are nearly the same in the TTHM being 109 μg/ℓ and 117 μg/ℓ, respectively. However, the value is slightly better in Case No. 4 because of the addition of powdered activated carbon.

Fig. 3-1 Condition and Results of Simulation Test No. 1
(Pre Chlorination)



	Feeding Point & Feeding Rate (mg/1)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	–	–	10	30	–	–	–	–

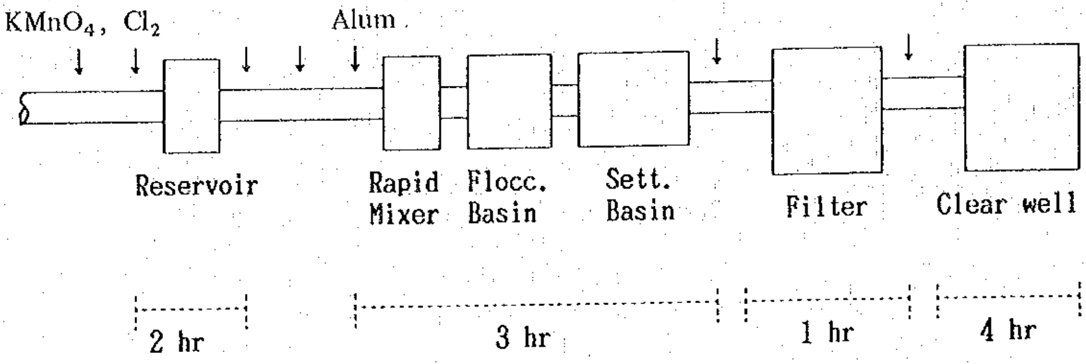
(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	6	8	17	12
$CHCl_2Br$	12	28	38	52
$CHClBr_2$	20	28	50	52
$CHBr_3$	16	16	28	27
TTHM	54	80	133	143

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	8.07	4.7	3.0	0.061	62
Clorination Water(4days)	8.11	–	3.1	0.042	47

P V: Potassium permanganate consumption value
C L: Chemi. Luminescence absorbance

Fig. 3-2 Condition and Results of Simulation Test No. 2
(Pre. Cl_2 (I) – $KMnO_4$ treatment)



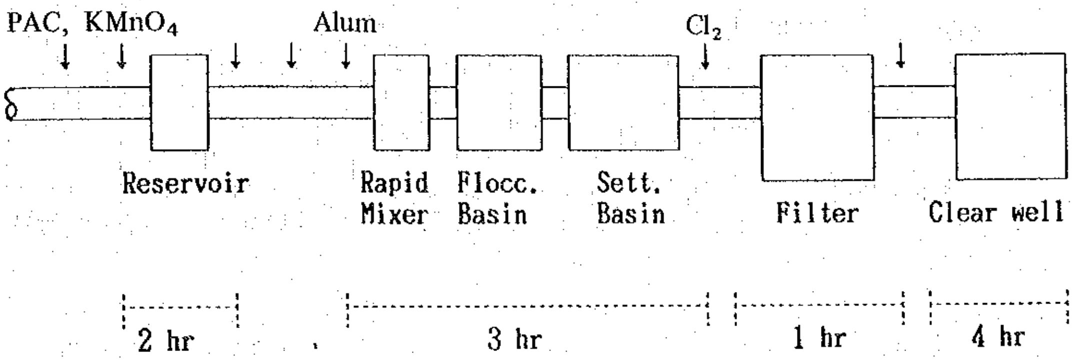
	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	–	1.0	10	30	–	–	–	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	6	8	15	14
$CHCl_2Br$	12	22	37	42
$CHClBr_2$	22	34	54	53
$CHBr_3$	18	22	33	32
TTHM	58	86	139	141

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	8.04	4.6	2.8	0.056	61
Clorination Water(4days)	8.04	–	2.9	0.047	56

Fig. 3-3 Condition and Results of Simulation Test No. 3
(Powdered Activated Carbon – $KMnO_4$ – Intermediate Chlorination)



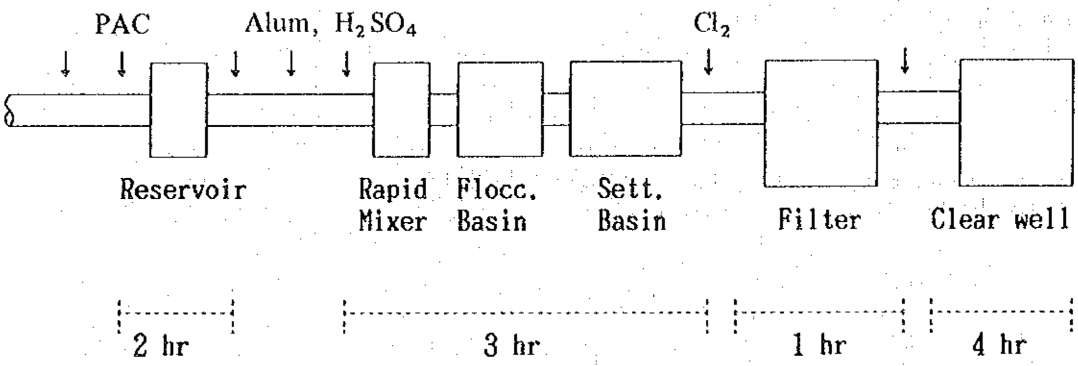
	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	10	1.0	–	30	–	–	8.5	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	4	6	7	3
$CHCl_2Br$	14	22	30	29
$CHCl Br_2$	34	48	67	74
$CHBr_3$	40	60	77	82
TTHM	92	136	181	189

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	7.58	3.5	2.5	0.050	60
Clorination Water(4days)	8.48	–	2.5	0.036	43

Fig. 3-4 Condition and Results of Simulation Test No. 4
(PAC – Low pH Coagulation – Inter. Cl_2)



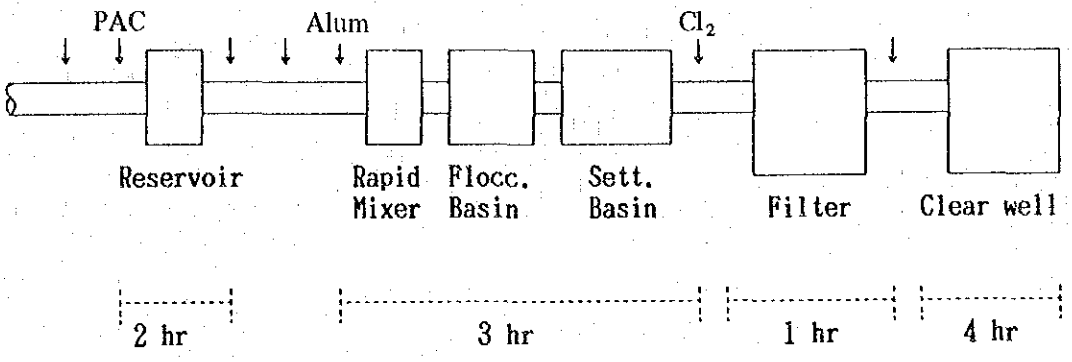
	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	10	–	–	80	–	–	8.5	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	4	4	7	3
$CHCl_2Br$	10	16	25	24
$CHClBr_2$	22	26	45	51
$CHBr_3$	12	12	23	31
TTHM	48	58	100	109

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	6.54	3.6	2.3	0.053	49
Clorination Water(4days)	8.10	–	2.3	0.033	25

Fig. 3-5 Condition and Results of Simulation Test No. 5
(PAC – Inter. Cl_2)



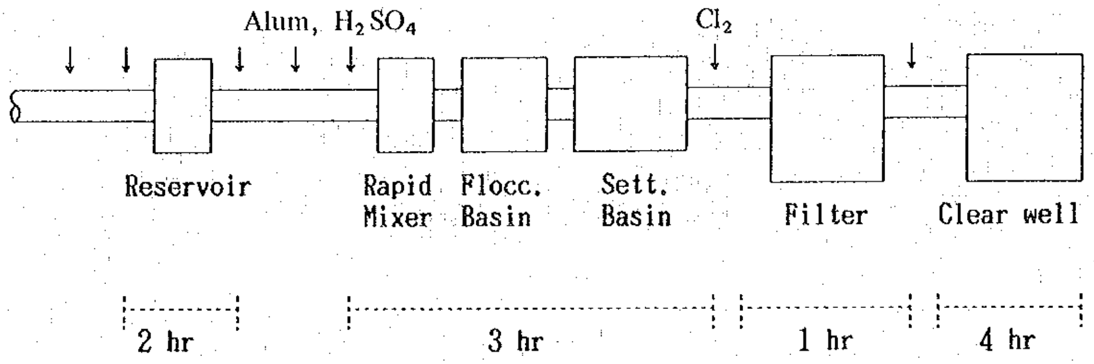
	Feeding Point & Feeding Rate (mg/1)							
	Reservoir			Rapid Mixer			Filter	C.well
	PAC	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	10	–	–	30	–	–	8.5	–

(µg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	4	10	18	20
$CHCl_2Br$	16	30	52	56
$CHClBr_2$	40	60	92	95
$CHBr_3$	46	62	83	86
TTHM	106	162	245	257

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	7.56	4.3	2.4	0.058	60
Clorination Water(4days)	8.52	–	2.9	0.046	54

Fig. 3-6 Condition and Results of Simulation Test No. 6
(Low pH – Int. Cl_2)



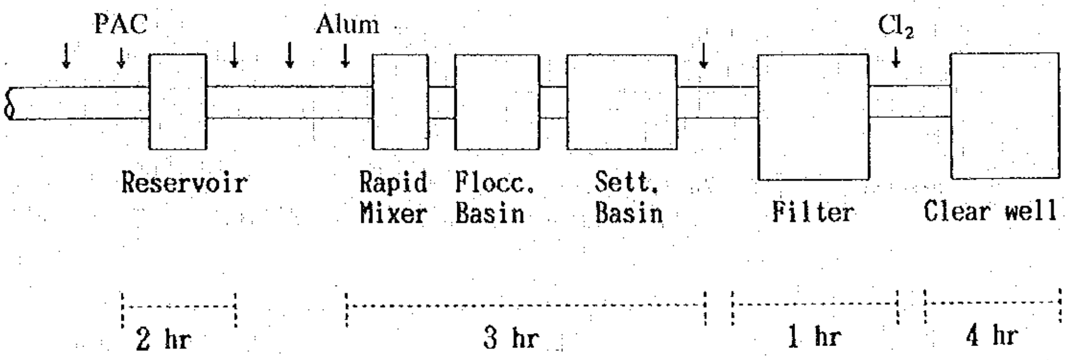
	Feeding Point & Feeding Rate (mg/1)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	–	–	–	30	80	–	8.5	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	2	4	8	4
$CHCl_2Br$	6	16	28	28
$CHClBr_2$	14	32	53	55
$CHBr_3$	8	20	29	30
TTHM	30	72	118	117

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	6.62	3.6	2.5	0.058	57
Clorination Water(4days)	7.96	–	2.2	0.034	30

Fig. 3-7 Condition and Results of Simulation Test No. 7
(PAC – post Chlorination)



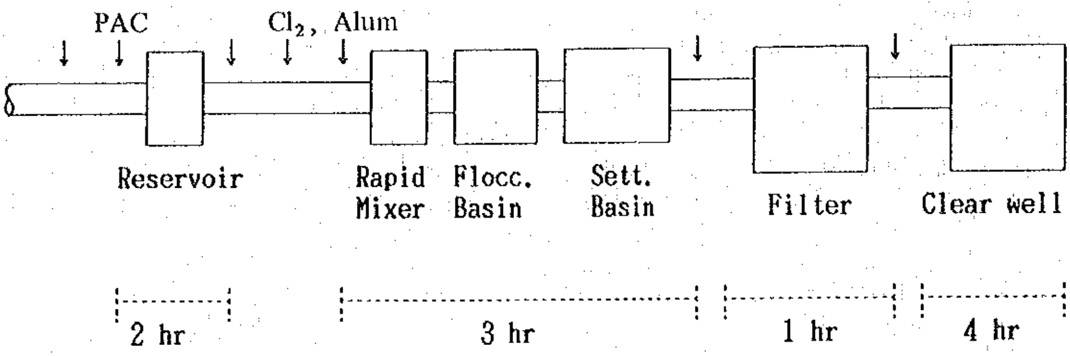
	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	10	–	–	30	–	–	–	8.5

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	4	4	4	5
$CHCl_2Br$	14	20	34	35
$CHClBr_2$	32	42	70	72
$CHBr_3$	36	50	80	81
TTHM	86	116	188	193

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	7.59	5.4	3.2	0.056	60
Clorination Water (4days)	8.54	–	3.2	0.043	40

Fig. 3-8 Condition and Results of Simulation Test No. 8
(PAC – pre Chlorination)



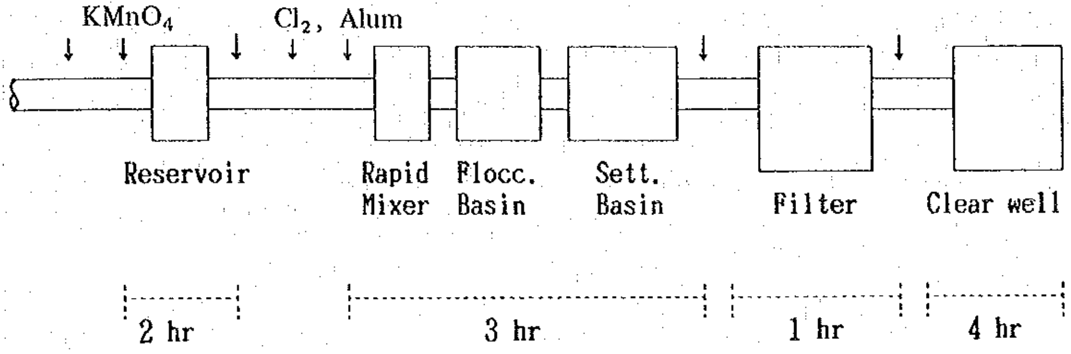
	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	PAC	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	10	–	–	30	–	10	–	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	4	8	13	7
$CHCl_2Br$	14	26	44	42
$CHClBr_2$	30	46	70	71
$CHBr_3$	28	42	59	57
TTHM	76	122	186	177

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	8.77	4.6	2.9	0.064	63
Clorination Water (4days)	8.80	–	2.9	0.042	51

Fig. 3-9 Condition and Results of Simulation Test No. 9
($KMnO_4$ – pre Cl_2)



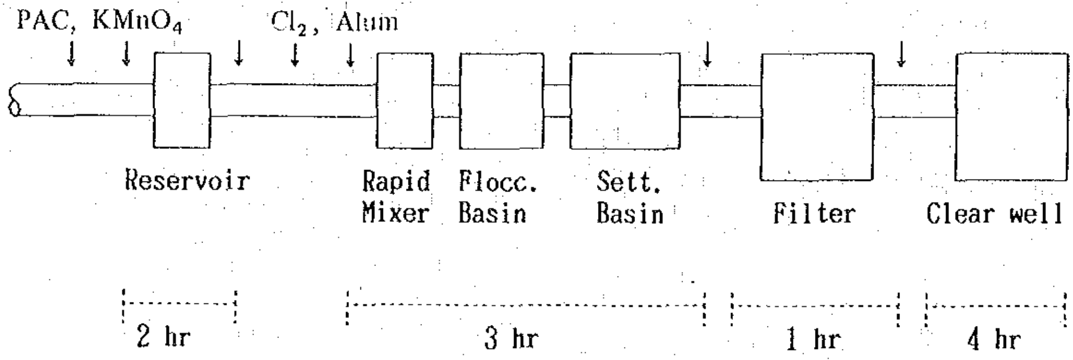
	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	–	1.0	–	30	–	10	–	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	6	10	16	12
$CHCl_2Br$	12	30	43	43
$CHClBr_2$	26	54	67	68
$CHBr_3$	22	48	55	56
TTHM	66	142	181	179

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	8.73	3.2	2.9	0.066	71
Clorination Water(4days)	8.76	–	2.8	0.042	53

Fig. 3-10 Condition and Results of Simulation Test No. 10
($PAC - KMnO_4 - pre\ Cl_2$)



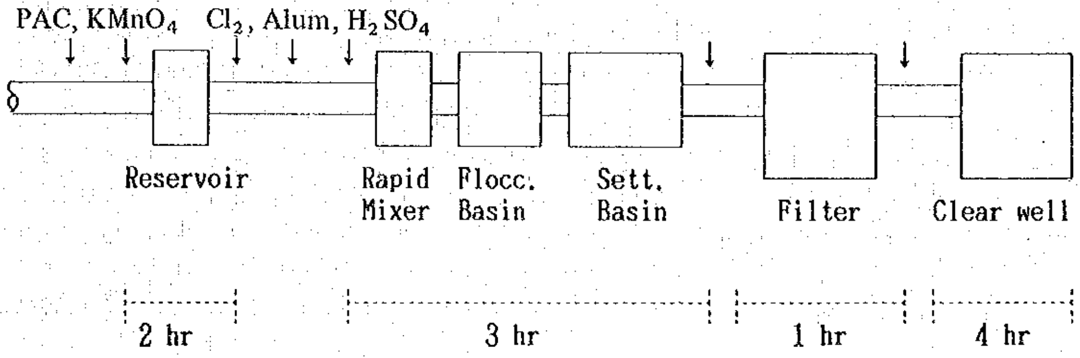
	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	10	1.0	–	30	–	10	–	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	4	8	8	8
$CHCl_2Br$	12	24	30	33
$CHClBr_2$	26	46	56	54
$CHBr_3$	26	44	51	48
TTHM	68	122	145	143

	p H	P V	DOC	U.V	C L
Clorination Water (1hr)	8.76	4.3	2.8	0.057	62
Clorination Water(4days)	8.59	–	3.1	0.043	46

Fig. 3-11 Condition and Results of Simulation Test No. 11
(PAC – $KMnO_4$ – pre Cl_2 – Low pH)



	Feeding Point & Feeding Rate (mg/l)							
	Reservoir			Rapid Mixer			Filter	C.well
	P A C	$KMnO_4$	Cl_2	Alum	H_2SO_4	Cl_2	Cl_2	Cl_2
mg/ℓ	10	1.0	–	30	80	10	–	–

(μg/ℓ)

	after 6 hr	24 hr	48 hr	96 hr
$CHCl_3$	4	6	6	2
$CHCl_2Br$	6	14	24	27
$CHClBr_2$	10	18	37	39
$CHBr_3$	6	8	16	17
TTHM	26	46	83	85

	pH	PV	DOC	UV	CL
Clorination Water (1hr)	7.20	3.6	2.8	0.051	48
Clorination Water(4days)	7.51	–	2.5	0.034	27

Table 3-1 Results of Simulation Test

No.	Treatment Process	Feeding Point & Feeding Rate (mg/ℓ)								pH	1. $CHCl_3$ 2. $CHCl_2Br$ 3. $CHClBr_2$ 4. $CHBr_3$ 5. TTHM	THM (µg/ℓ)				Others (Rank)
		Reservoir			Flush Mixer			Filter	Clear Well			After 6 hr	24 hr	48 hr	96 hr	
		PAC	$KMnO_4$	(I) Cl_2	Alum	H_2SO_4	(II) Cl_2	Cl_2	Cl_2							
1.	Pre. Cl_2	–	–	10	30	–	–	–	–	8.07	1.	6	8	17	12	(6)
											2.	12	28	38	52	
											3.	20	28	50	52	
											4.	16	16	28	27	
											5.	54	80	133	143	
2.	Pre. Cl_2 (I) $KMnO_4$	–	1.0	10	30	–	–	–	–	8.04	1.	6	8	15	14	(4)
											2.	12	22	37	42	
											3.	22	34	54	53	
											4.	18	22	33	32	
											5.	58	86	139	141	
3.	PAC $KMnO_4$ Int. Cl_2	10	1.0	–	30	–	–	8.5	–	7.58	1.	4	6	7	3	(9)
											2.	14	22	30	29	
											3.	34	48	67	74	
											4.	40	60	77	82	
											5.	92	136	181	189	
4.	PAC Low pH Int. Cl_2	10	–	–	30	80	–	8.5	–	6.54	1.	4	4	7	3	(2)
											2.	10	16	25	24	
											3.	22	26	45	51	
											4.	12	12	23	31	
											5.	48	58	100	109	
5.	PAC Int. Cl_2	10	–	–	30	–	–	8.5	–	7.56	1.	4	10	18	20	(11)
											2.	16	30	52	56	
											3.	40	60	92	95	
											4.	46	62	83	86	
											5.	106	162	245	257	
6.	Low pH Int. Cl_2	–	–	–	30	80	–	8.5	–	6.62	1.	2	4	8	4	(3)
											2.	6	16	28	28	
											3.	14	32	53	55	
											4.	8	20	29	30	
											5.	30	72	118	117	
7.	PAC Post Cl_2	10	–	–	30	–	–	–	8.5	7.59	1.	4	4	4	5	(10)
											2.	14	20	34	35	
											3.	32	42	70	72	
											4.	36	50	80	81	
											5.	86	116	188	193	
8.	PAC Pre. Cl_2 (II)	10	–	–	30	–	10	–	–	8.77	1.	4	8	13	7	(7)
											2.	14	26	44	42	
											3.	30	46	70	71	
											4.	28	42	59	57	
											5.	76	122	186	177	
9.	$KMnO_4$ Pre. Cl_2 (II)	–	1.0	–	30	–	10	–	–	8.73	1.	6	10	16	12	(8)
											2.	12	30	43	43	
											3.	26	54	67	68	
											4.	22	48	55	56	
											5.	66	142	181	179	
10.	PAC $KMnO_4$ Pre. Cl_2 (II)	10	1.0	–	30	–	10	–	–	8.76	1.	4	8	8	8	(6)
											2.	12	24	30	33	
											3.	26	46	56	54	
											4.	26	44	51	48	
											5.	68	122	145	143	
11.	PAC $KMnO_4$ Pre. Cl_2 (II) Low pH	10	1.0	–	30	80	10	–	–	7.20	1.	4	6	6	2	(1)
											2.	6	14	24	27	
											3.	10	18	37	39	
											4.	6	8	16	17	
											5.	26	46	83	85	

Pre. Cl_2 : Pre Chlorination, $KMnO_4$: $KMnO_4$ treatment, PAC : Powdered Activated Carbon
Int. Cl_2 : Intermediate Chlorination, Low pH : Low pH Coagulation, Post Cl_2 : Post Chlorination

(5) Case No. 7

In Case No. 7, the sample was post-chlorinated following the addition of PAC, in an attempt to reduce the THM formation potential. Normally the THM formation potential should have been reduced considerably by this kind of treatment, but we observed nevertheless that the THM formation stood higher than in the case of coagulation at a low pH.

From the above cases it became necessary to check the quality of the PAC (Norit W-20) obtained at the Zay Purification Plant against the Japanese product (KINTOL). As the result of performance test in Japan, we found out that the capability of Norit W-20 was approximately 50 % lower than that of Japanese Kintol in regard to the removal of THM formation potential, as shown in Appendix 2. In this connection, we propose that an adequate step be taken on the part of Zay personnel either to use more dose of Norit W-20 or to obtain a better quality of powdered activated carbon which necessitates change in the purchase specification. For reference, Japanese specifications are given in Table 3-2 below.

Table 3-2 Selection Standard of Powder Activated Carbon (JWWA K 113—1974)

Item	Selection standard	Specification
Grain size	Surplus less than 10% after 74 μ screening	100 mesh
Methylene blue decoloration	—	More than 150 ml/g
Iodine adsorption	—	More than 1,000 mg/g
Dry weight reduction	20~50%	45~50%
pH value	4~11	4~11
Chloride	Less than 0.5%	Less than 0.5%
Lead	Less than 10 ppm	Less than 10 ppm
Zinc	Less than 50 ppm	Less than 50 ppm
Cadmium	Less than 1 ppm	Less than 1 ppm
Arsenic	Less than 2 ppm	Less than 2 ppm
Conductivity	Less than 900 μ℧/cm	—

Further about Norit W-20, it is found that the moisture ratio of it is very low as 2 %. Therefore, much trouble is anticipated while it is added into water at Zay plant as the powder would be flying about. Most of the Japanese products are about 50 % in the moisture ratio. Anyway, this problem has to be tackled from different aspects including transportation costs.

(6) Cases No. 8 and No. 9

These are such that we compared the cases using PAC and pre-chlorination against the dosing of $KMnO_4$ with pre-chlorination. No difference of noteworthy is seen in the THM formation between the two cases.

(7) Cases No. 9 and No. 10

$KMnO_4$ was dosed and pre-chlorination was made in Case No. 9 and PAC was used additionally in Case No. 10. In Case No. 10, a reduction of 20 to 30 % was observed in the THM formation owing to the PAC.

(8) Cases No. 10 and No. 11

In addition to the combination in Case No. 10, coagulation at a low pH was initiated in Case 11. As the result, it was noticed that the THM formation was about 50 % less.

3-2 Evaluation of Case No. 11

Among the above 11 cases, the TTHM formation is the smallest in Case No. 11 due to the fact that all of powdered activated carbon, $KMnO_4$ and chlorine are added. Although the method in Case No. 11 is best, it is difficult to employ this in its entirety for reasons such as given below.

(1) Trouble Caused by Excessive Dose of $KMnO_4$

In the present test series using $KMnO_4$, when a dose was in excess of 1.0 mg/ℓ, the color of it remained even after coagulation. From this, it is known that control should be made over the dose of $KMnO_4$ not to exceed 1.0 mg/ℓ. In other tests using the same, when a dose was given at 1.0 mg/ℓ, the TTHM formation became larger than in the case of no dose, and with a dose of 3.0 mg/ℓ, the condition of TTHM formation became at last a little better.

In view of the above, it is considered not to use $KMnO_4$ as long as it means to reduce the amount of THM formation.

(2) Prechlorination and Intermediate Chlorination

Again, Case No. 4 is the combination of three elements – PAC, coagulation at a low pH and intermediate chlorination, while Case No. 11 has four – PAC, coagulation at a low pH, dosing of $KMnO_4$ and prechlorination. When the dosing of $KMnO_4$ is disregarded for the reason mentioned in (1) above, the only difference is whether intermediate chlorination or prechlorination, by which the difference in the TTHM became 109 μg/ℓ and 85 μg/ℓ, respectively. From this, it is evident that prechlorination is more effective in reducing TTHM.

However, when one makes a careful examination over the characteristics of prechlorination and intermediate chlorination as given below, we can hardly say that prechlorination is better.

Intermediate chlorination is recommended by EPA of USA for the reason that it is effective to inhibit formation of THM, for it is able to remove the precursor to some extent at some stages of coagulation and sedimentation.

Even though 40 – 50 % of the precursor is removable by coagulation and sedimentation, that does not necessarily mean that the formation of THM is reducible by 40 – 50 %. In reality, the reduction rate through intermediate chlorination is presumably about 10 – 20 % in most cases, because of the existence of total organic chlorine as graphically illustrated in Fig. 3-12.

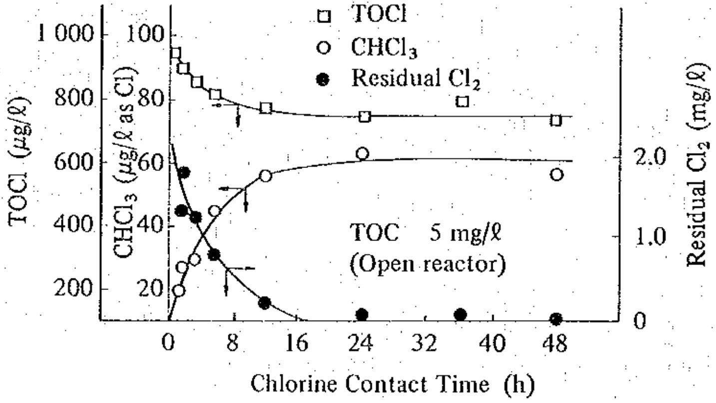


Fig. 3-12 THM and TOCl formation pattern of Peat soil water

Reference to the above diagram, total organic chlorine '□' completes its formation in a very short time after chlorine is added to raw water. After this, part of the total organic chlorine changes slowly to THM 'O' while hydrolyzing. Thus, the rate of THM formation rises as the time goes by. Total organic chlorides has a relatively large molecular weight in many cases which is easily removable by coagulation and sedimentation. As such, intermediate chlorination is finished in one to two hours after chlorine addition.

In the prechlorinated state, however, part having a large molecular weight of total organic chlorine is removed by sedimentation. So, reduction to some degree of the THM is possible even through prechlorination. However, the effect of THM reduction through prechlorination or intermediate chlorination seems to be not so high as the effect of precursor removal which is obtainable by coagulation and sedimentation.

Total organic chloride does hydrolyze with the lapse of time and change to THM. So, if the coagulation sludge is left unattended for a long time after prechlorination, it would possibly discharge THM into the precipitation liquid.

As described above, the control effect in prechlorination or intermediate chlorination varies depending on the quality of raw water or on the purification condition. So, it is impossible to say what effect is obtainable in general. However, as there are many examples from which it is known that intermediate chlorination is more effective than prechlorination in reducing THM formation by 10 – 40 %, it is recommended that simulation tests be made again to further confirm the given data.

From the foregoing, it is understood that Cases No. 4 and No. 11 are most effective. And, when these two cases are compared, the method used in Case 4 seems better for the reason that prechlorination does not seem to be a good method for reducing THM in general as mentioned already, and color control is difficult in regard to the use of $KMnO_4$ with no effective result in THM reduction. So, the best one is the combination of powdered activated carbon, coagulation at a low pH and intermediate chlorination.

4. Recommended THM Reduction Measures at Zay Plant

In this Chapter, we present some practical measures which can be applied at the Zay Water Purification Plant for reducing TTHM from the drinking water. In this connection, we use the simulation test data of the East Ghor Canal raw water samples which we brought back to Japan.

4-1 Measures under Existing Purification System

As described in the previous chapter concerning the simulation test results, the most effective method available from the data is considered to be such combination of processes, namely, coagulation at low pH, dose of powdered activated carbon and intermediate chlorination. Since intermediate chlorination requires no reconstruction of the existng equipment, we deal now with the other two problems.

1) Coagulation at Low pH

(1) Effect of pH Control

Figs. 4-1, 2 and 4-3 below show the effect of THM removal by pH control which have been made public in Japan.

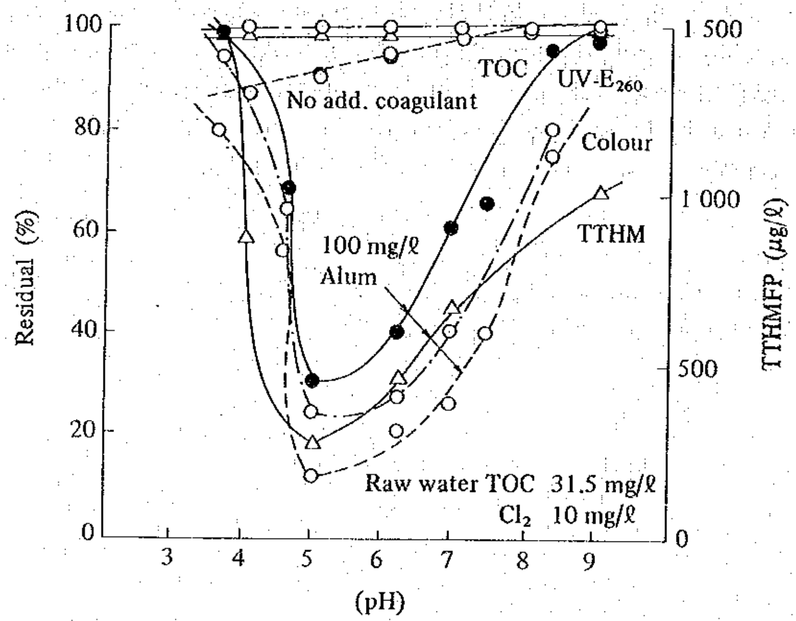


Fig. 4-1 Removability of THMFP and Organic Substances by Coagulation, Settling and Filtration (Aizawa, Magara)

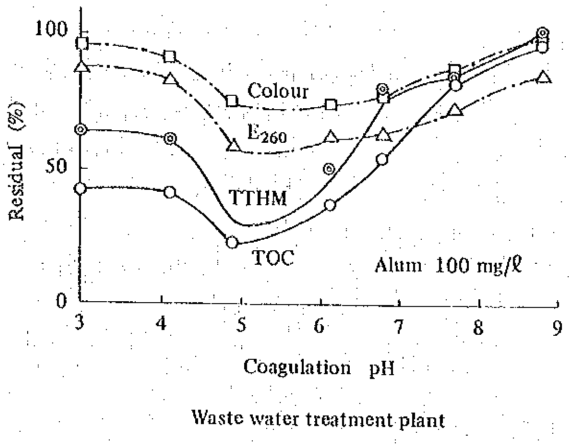


Fig. 4-2 Coagulation map of waste water treatment plant water

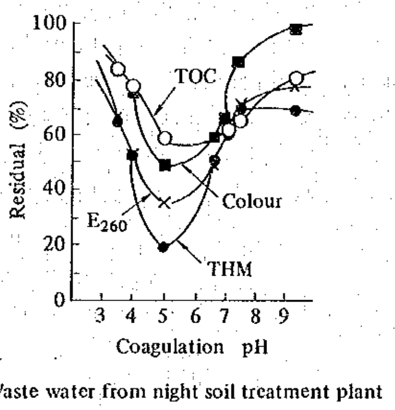


Fig. 4-3 Coagulation map of night soil treatment plant water

THM formation varies by pH. The data shown on these charts are test examples of the removability of THM precursors when peaty land water, biologically treated waste water and treated night soil are coagulated and settled by the use of alum under changing pH.

As seen, the removal effect of organic substances becomes highest at about pH 5–6 and at the same time the THM formation potential reduces in the like pattern in each example.

The average pH of the water taken at Deir Alla is as high as 8.10, so that no one can expect a substantial THM reduction effect of the water, as seen from the examples. Accordingly, we consider that if an alteration is made of the equipment as to lower pH in coagulation, some effect would be attainable.

(2) Results of Simulation Tests

The effect as given in Case 4 of simulation tests is attributed to the combined process – injection of powdered activated carbon, coagulation at low pH and intermediate chlorination. As regards the pH lowering, we injected 80 mg/ℓ sulfuric acid, thus keeping the pH at about 6.5 for coagulation, so that we could reduce the THM to 109 μg/ℓ after 96 hours, approximately 40 % of the worst 257 μg/ℓ in Case 5, as seen in Table 3-1.

As of Cases No. 6 and No. 11 in which we also used low pH, the results were 117 μg/ℓ and 85 μg/ℓ, respectively, indicating that the coagulation at low pH is effective in reducing THM. In each case, we used a substantially large amount of sulfuric acid as 80 mg/ℓ.

(3) Additional Installation of a Sulfuric Acid Injector

A. Possibility for Substitute Use of Existing Pump

As there is no sulfuric acid injection pump existing at the Zay Plant, we checked a possibility to use any of the existing pumps for this purpose. The one that drew our attention is the caustic soda injection pump as there is no need for alkalizing. (Apart from the problem of chemical resistance of the pump.) However, we found it inadequate due to the fact that the injection capacity is so small as 10 mg/ℓ.

As such, the only way left in this connection would be to purchase a pump useful for sulfuric acid injection or to provide a tank of gravity flow-down type. Moreover, it would be necessary to install a storage tank to accommodate a large quantity of sulfuric acid.

Of the proposed storage tank, the capacity should be about 70 tons according to the following formula, provided that the supply of sulfuric acid be taken weekly and a maximum injection quantity be 80 mg/ℓ, if possible under the local supply condition;

$$80\ \text{g/m}^3 \times 123{,}000\ \text{m}^3/\text{day} \times 7\ \text{days} = 68.88\ \text{tons} \fallingdotseq 70\ \text{tons}$$

Suppose the dimensions of the tank be 5 m x 5 m x 3 m, the capacity would be 75 tons (with a margin). A plastic tank of this size would cost approximately 6 million yen, according to the Japanese market price.

B. Injection Device

The gravity flow-down injection system requires installation of a storage tank in the vicinity of the raw water regulation reservoir, and a flow regulation valve on the tank to let sulfuric acid flow down and drop into the reservoir. An advantage of this system is the simpleness in the construction of the device. However, there are some disadvantages involved in this system such as that the drops may not be well mixed with the water in the reservoir because of the gravity flow-down mode and frequent check is required over the injection quantity following change of the fluid level in the tank as time goes by. (Manual control of injection quantity would be inexpensive) However, the latter problem could be solved if the tank would be placed higher or if an automatic regulation valve would be provided on the tank, though an extra cost would ensue.

In this respect, we give cost estimates as follows according to Japanese market prices:

– When the tank is raised:

Tank:	¥6,000,000
Valves and Pipings	¥ 500,000
Frames:	¥2,000,000
TOTAL	¥8,500,000

– When a regulation valve is installed on the tank

Tank:	¥6,000,000
Regulation Valve with flowmeter	¥2,500,000
Frames:	¥1,000,000
TOTAL	¥9,500,000

– Cost of Sulfuric Acid: @¥23 per kg

$$80\ \mathrm{g/m^3} \times 123{,}000\ \mathrm{m^3/day} \times \frac{1}{1000} \times ¥23/\mathrm{kg} =$$

¥226,320 per day (Equivalent to approximately US$1,000 per day)

On the other hand, the pump injection system is advantageous that a tank installation site can be optionally selected and injection can be made to a point in the reservoir where the best mixing effect is obtainable. However, this would require rearrangements with respect to the existing electric, instrumental and other associated facilities. The total cost in conjunction with the pump injection system would be as follows according to our estimation:

Tank:	¥6,000,000
Pump with flow regulating system:	¥1,500,000
Valves and Pipings:	¥1,500,000
Electric and instrumental:	¥1,000,000
TOTAL	¥10,000,000

By comparing the above two cases, we recommend the latter (the pump injection system) because it is more effective for accurate control.

C. Remarks about Injection Point

In either of the gravity flow-down system and the pump injection system, it would be necessary to choose an adequate point in order to attain a sufficient stirring effect. The point in question should be where the flow rate is highest, that is either into the induction tube leading to the reservoir or into part of the reservoir by piping close to its outlet.

D. Materials

As regards the material for the tank, we consider it adequate to use SUS316 or plastic or rubber lined one when the fluid used is undiluted sulfuric acid of 98 % concentration. If sulfuric acid to be used is less than 98 % in concentration, SUS316 would be of no use due to higher corrosion rate.

As for piping to the tank, a material like vinyl chloride or rubber lining is most suitable, and as for the portions to contact the fluid of the pump, flowmeter and regulating valve, it would be necessary to specify a material of chemical resistance.

E. Installation of pH Meter

For confirming the pH control effect, it is necessary to measure a pH value at an appropriate point of the reservoir after injecting sulfuric acid. As regards pH meter, it would be very simple to install one of permeation type on the back side of the rapid mixer. In this case, it would be necessary to lay cable for the transmission of measurement signal to the control station. The total cost for the installation of a pH meter is estimated as follows:

pH meter:	¥1,000,000
Cabling:	¥ 200,000
TOTAL	¥1,200,000

F. Total Cost

The total of all the costs given above covering the installation of a new storage tank, the pump injection system and the installation of a pH meter would be around ¥11,200,000, according to the Japanese market prices.

The cost of sulfuric acid would be:

¥226,320 per day (equivalent to approximately US$1,000)
¥1.84 per cubic meter (equivalent to approximately US 0.8 cent)

2) Powdered Activated Carbon (PAC)

The fact that the PAC used in the simulation test series was not very effective seems to attribute to an inferior quality of it. However, the effect of PAC is undeniable, so combined application of it is recommended. The more the PAC, the more desirable it is to gain a better effect. But, the PAC is an expensive material. Therefore, 30 mg/ℓ seems to be practical and 50 mg/ℓ seems to be the limit.

A. Information about Powdered Activated Carbon in Japan

Presently, 23,000 tons of PAC is consumed annually in Japan and much of the PAC is made from sawdust by chemical treatment or by steam activation after heating. Of the production, approximately 22 % or 5,000 tons is made by chemical treatment and the rest (78 %) or 18,000 tons by steam activation. Beside sawdust, coconut husk can also be used. The Japanese domestic price of the PAC is ¥550 – 650 per kg (equivalent to US$2,400 to 2,900 per ton) in a dry state (moisture content: 0 %). An Indian product is about US$800 per ton, though the quality is inferior.

B. Possibility of Domestic Production in Jordan

As PAC is expensive, it is desirable to produce it domestically when a large consumption is expected. If sawdust is available in a large quantity, that is most suitable. Coconut husk is useful, too. Besides, a study about using wheat husk is under way, but this is not materialized yet.

C. Cost for PAC Increase

The price of dry powdered activated carbon is estimated at ¥600 per kg (¥0.6 per gram). Besides, the cost for enlarging the capacity of the existing PAC injection equipment seems to be indistinct, but, anyway, it is estimated at ¥3 million.

When the injection rate is 10 mg/ℓ: 10 g/m^3 x ¥0.6/g = ¥ 6/m^3 . . ¥ 738,000 per day
When it is 20 mg/ℓ: 20 g/m^3 x ¥0.6/g = ¥12/m^3 . . ¥1,476,000 per day
When it is 30 mg/ℓ: 30 g/m^3 x ¥0.6/g = ¥18/m^3 . . ¥2,214,000 per day

4-2 Introduction of Granular Activated Carbon (GAC)

It is alleged that the GAC treatment is an effective method for removal of THM formation potential and THM. For practical application of GAC, however, deliberate assessment and investigation together with experiment should be made in advance. In the followings we explain test methods, reactivation methods, treatment costs and other as well as our opinion with regard to the effectiveness of GAC.

In our opinion, GAC should be introduced when the total THM is not be decreased to a desired level in spite of the ways and means mentioned in before mentioned.

1) Effectiveness of GAC

Here we describe briefly about the effectiveness of GAC in accordance with some practical and experimental examples. THM reduction techniques including the use of GAC are described in details in "Treatment Techniques For Controlling Trihalomethanes In Drinking Water (presented to Dr. Abdulhamid Khatib of Water Laboratories, Water Authority of Jordan)".

However, we confine our explanation to the scope of Japanese research cases.

The treatment effects about river water are such as shown in Fig. 4-4 and Fig. 4-5. Fig. 4-4 is an example of THM removal by GAC after river water is first prechlorinated and then coagulated and settled. Fig. 4-5 is an example of THM removal by GAC after river water is first coagulated and settled and then intermediate-chlorinated and sand filtered.

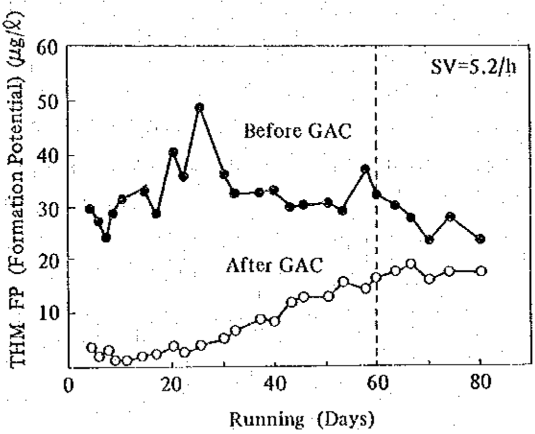


Fig. 4-4 Prechlorination – Coagulation – Sedimentation – GAC Filtration (River Water)

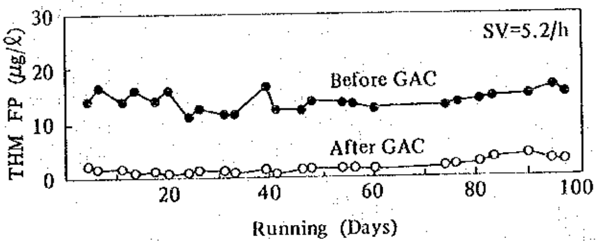


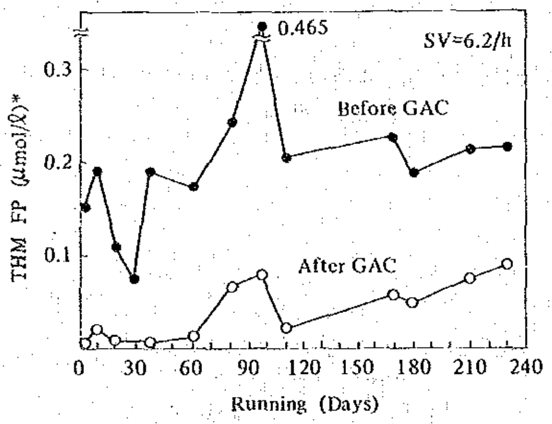
Fig. 4-5 Coagulation – Settling – Intermediate Chlorination – Sand Filter – GAC Filter (River Water)

According to the above data in Fig. 4-4 using prechlorination, chloroform formed through prechlorination (not shown) and total THM become unremovable at all in 53 days and in 60 days, respectively, when the water is processed at a 5.2 m of space velocity per hour. Also, as shown in Fig. 4-4, THM formation potential removal rate drops to below 50 % in approximately 60 days. However, as the break through of brominated trihalomethanes is later than chloroform, the life of GAC filter at the Zay plant is assumed to be longer than that shown in Fig. 4-5.

Fig. 4-5 gives the data obtained by GAC treatment of river water in intermediate chlorination. Unlike the data in Fig. 4-4, the THM removal rate remains still high even in about 100 running days.

From these data, it is considered necessary to shorten the period as much as possible from chlorination to GAC filtration. In other words, intermediate chlorination is better than prechlorination in obtaining THM reduction effects.

In the foregoing, we referred to typical examples of process ability by comparing prechlorination and intermediate chlorination on the assumption that GAC is used instead of anthracite in the existing rapid filter. In the case, however, an additional absorption filter would become necessary for removal of precursors, which would require an comprehensive study concerning such matters as removal effect, structure of a new filter and hydraulic condition.



* THM 1 μmol/ℓ = 11.9 μg $(CHCl_3)$/ℓ

Fig. 4-6 GAC treatment for THMFP removing
(River Water)

Fig. 4-6 shows a test example in which river water is filtered directly through GAC in an attempt to remove presursors. As seen, the removal rate still keeps 60 % even in as long as 240 days.

As above, we described briefly about the effectiveness of GAC, and we now conclude that there are two alternative methods of using GAC for effective treatment; either in filtering raw water to remove precursors or in removing formed THM after intermediate chlorination. When consideration is given about the present flow system at the Zay Plant, the best feasible way without requiring an extensive remodelling on the existing structure seems to be the latter, that is, to filter coagulated water by way of GAC after intermediate chlorination. If this idea is practical, then the anthracite now in the rapid filter should be replaced by GAC.

In the followings we describe various matters including test method regarding the introduction of GAC to the Zay Water Purification Plant.

2) The Contents of Pilot Plant Test

For this purpose, a long-range plan should be made after investigating relevant problems such as the difference in performance by types of activated carbon, the removability and life of activated carbon, washing method and layer thickness.

(1) Type of Activated Carbon

There are coal, coconut husk, petroleum pitch and some others which serve as materials for the production of activated carbon. For removal of the precursors having a large molecular weight like humic substance, activated carbon of a type which has relatively adsorption pores as 3 – 20 nm is useful. For this, GAC made from coal which has a large proportion of 3 – 20 nm pore diameter is generally considered better suited than the GAC made from coconut husk because the latter's pore diameter is smaller. But, there are some data available to the contracy, so this problem should be tackled carefully.

As the GAC made from petroleum pitch is high in hardness and difficult to break off, it would be possible to specify a pore distribution and grain size to some degree.

The adsorption capacity of activated carbon is disproportional to the grain size of it. Therefore, the smaller the grain size, the larger the adsorption capacity GAC becomes. However, when a view is given about replacement of anthracite by GAC, we think it no good to use a small grain size for the reason that the height from the activated carbon surface to the overflow trough of existing filter is already fixed, permitting no reduction in the backwash velocity.

In selecting one from among the types of activated carbon, the followings should be checked in advance:

- The difference in adsorption capacity in regard to different types of material.
- The difference in adsorption capacity by grain sizes.
- The hardness of GAC, and the recovery rate and the residual adsorption capacity in case of generation

(2) Investigation of Hydraulic Properties of Filter

As mentioned above, the smaller the grain size, the larger the adsorption capacity, but contrarily the water head loss becomes larger. Since carbon of smaller grain size tends to flow out during backwash, it is inevitable to use carbon of relatively large grain size at the sacrifice water energy.

In this case, the followings should be checked:

- The expansion rate in backwash by different types of carbon in respect of grain size distribution. (The expansion rate is limited by the height of the trough, unless it is raised. Since the expansion rate varies by water temperature, it is recommended to check it when the temperature is low.)

- The variation of water head loss between the cases of filter running and backwashing. (*This is to check a timing for backwashing.*)

(3) Equipment

For testing, transparent columns to be fabricated with acrylic resin by reference to the drawing shown in Fig. 4-7-1 shall be prepared. The preferred number of columns would be five or at least three.

Fig. 4-7-2 shows a skeletonized design of the filtration system in Fig. 4-7-1. The filtering column should be designed to have a height corresponding to the level of the trough in the existing filter.

Now, the essentials of the proposed test equipment which would comprise an sampling pump, a pressure tank and several adsorption columns are follows.

Of these, the sampling pump would have to be installed in the settling basin, but if the existing sampling system is useful, that would be unnecessary.

Each adsorption column should be so structured that the rise of the column to the overflow level from the GAC layer correspond to the overflow trough level from the anthracite layer in the rapid filtration pond. The pressure tank should be adjustable vertically to meet the depth of inlet water in the pond.

For easy feed of GAC into the column, it is recommended to make part of it detachable or to provide a hole around the middle part of it. For removal of GAC, it is recommended to provide a number of taps on the lower part of the column so that GAC could be washed out at backwash when the test is over. Flow regulation would be made by means of a valve installed on the bottom piping. For the measuring of a pressure loss, special pipings or differential pressure gauges of mercury column type would be installed on the top and bottom of the column.

What is very important here is the necessity of placing test equipment of this type in a dark place because if it is exposed to lights, algae and other microorganisms would grow on the surface of the GAC and, as a result, they would form of mud ball inside the column.

The total cost for five columns of this type would be about ¥6 million, according to the Japanese market price.

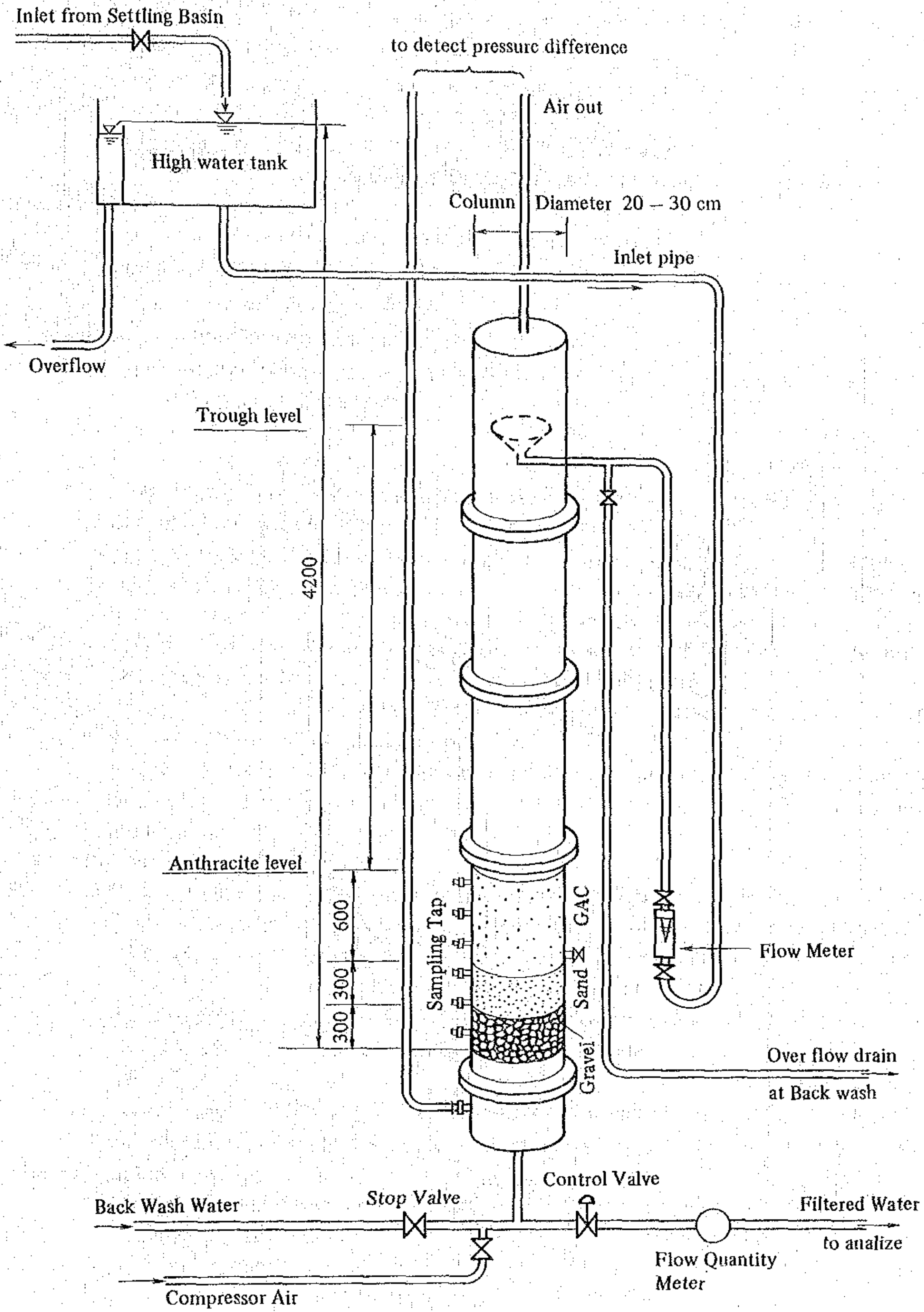

Inlet from Settling Basin
to detect pressure difference
Air out
High water tank
Column
Diameter 20 – 30 cm
Inlet pipe
Overflow
Trough level
4200
Anthracite level
600
300
300
Sampling Tap
GAC
Sand
Gravel
Flow Meter
Over flow drain
at Back wash
Control Valve
Back Wash Water
Stop Valve
Filtered Water
to analize
Flow Quantity
Meter
Compressor Air

Fig. 4-7-1

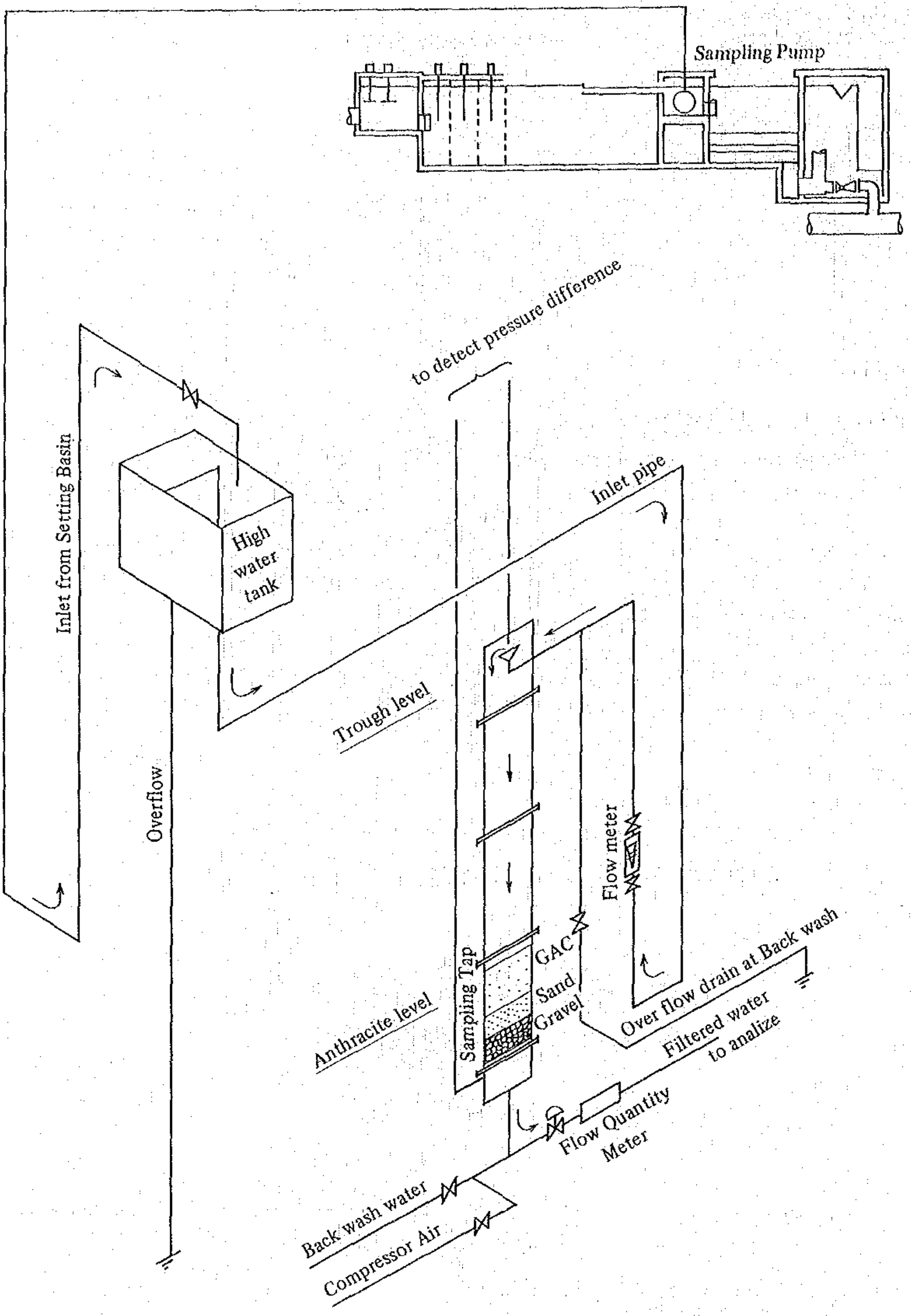

Sampling Pump
to detect pressure difference
Inlet from Setting Basin
High water tank
Inlet pipe
Trough level
Overflow
Flow meter
Sampling Tap
GAC
Sand
Gravel
Anthracite level
Over flow drain at Back wash
Filtered water to analize
Flow Quantity Meter
Back wash water
Compressor Air

Fig. 4-7-2

(4) Method of Pilot Plant Test Implementation

The test should be made in the following order:

(a) Procure activated carbon of different grain sizes from manufacturers.

(b) Check each type to make sure whether or not it can still be put to use again after backwash, with or without increasing the thickness of the layer.

(c) Check runout of GAC according to its grain sizes for comparison under simultaneous operation of filters.

(d) Pick out the best one and serve it for a long range test.

(e) Check the reactivation property of it.

Further about the above five steps:

(a) Procurement of Activated Carbon

- Get as many different types as possible in a total quantity equivalent to ten times the total capacity of the columns.

(b) Backwash

- Prepare anyone of the columns with anthracite in it which should comprise same filter composition of the existing rapid filter. This column should be regarded as control one with respect to other test columns.
- Prepare each of the other columns with GAC to a height equal to the anthracite level in the standard column, and do backwash in the like manner as performed in the existing filter to check the GAC run out from it or not.
- If GAC is seen not running out into the overflow water, then check the possibility of increasing the thickness of GAC layer in it and how much.
- From the above, it could be known as to what grain size which did not run out from the filter would be useful in practice.
- Besides, as there a kind of dust or fine carbon particles included in some types of GAC, it would also be necessary to check if anything like that is running out at backwash.

(c) Runout Rates

- Prepare each of the columns (other than the standard one) with the choice activated carbon and pass water simultaneously into all the columns. Then, take water samples from both ends of each column and check water qualities of influent and effluent. In this case, it would be allowed to set a water velocity faster than the actual filtration speed. But, if so done, backwash would have to be made more frequently due to higher resistance to the running water.
- After this, measurement should take place of many items about the inlet and outlet samples. THM and THM precursors are principal ones and others include the ultraviolet absorptivity, TOC, PV, dissolved oxygen, pH, water temperature and as many more as possible.
- The measurement should be carried out at least once a week, not necessarily everyday. At the same time, the quantity of filtrate and head loss by filter should be checked as well.
- When there are different types of good activated carbon, the test should be made separately as necessary. However, an attempt should be made each time to determine which one is best and more test made of it in a sufficient quantity to verify the usefulness of it.

- Backwash would be made about once a week as a rule and necessarily within the same day of the test.

(d) Long Range Test

- Prepare the standard column with a new supply of anthracite, and one of the test columns with the choice GAC and, if necessary, any of the others likewise, all with a thicker layer.
- Filter water at the same speed as used in the filter and do backwash several times in repetition at a regular interval.
- Measure those items, the same as mentioned in (c) above, at several times in repetition.
- Determine an active life of the treated GAC with the provision a margin according the filter running period.

(e) Regeneration Efficiency

- From the known active life from the above, it is possible to determine a regeneration cycle.
- Assuming that the filling hight of activated carbon is 0.60 m and the life of it 30 days:

Total fill-up: 0.60 m x 88.32 m^3/unit x 6 units
= 317,952 m^3 x 0.50 t/m^3* = 158,976 Tons ≒ 160 Tons
(* GAC Density)

From the above it is known that 5.3 tons of the used GAC would have to be reactivated everyday (160 tons ÷ 30 days)

3) Replacing Method and Cost

This is simply to remove anthracite and fill GAC in place of it, from one pond to another. As soon as replacement is finished, the pond involved should be backwashed and then water is filled. In most cases, no chemical treatment is made of GAC, so the pH of the water passing through may rise to as high as 11. Therefore, the water should be diluted through the other five ponds until its pH goes down to an adequate level before moving on the next pond.

The quantity of GAC required for filling each filter would be as follows, provided that the density of GAC be 0.5 ton/m^3:

88.32 m^3/unit x 0.6 m = 52,997 m^3 x 0.50 ton/m^3 = 26,496 tons/unit

The total for the six units plus a margin of two-pond equivalent would be:

26.496 tons/unit x 8 (6+2) = 211,968 = 212 tons.

In Japan, the GAC from coal is priced at ¥650,000 per ton, and the GAC from petroleum at ¥3 million per ton. Therefore:

GAC from Coal: 212 tons x ¥650,000 = ¥137.8 million
GAC from Petroleum: 212 tons x ¥3 m = ¥636 million

Activated carbon would lose 2 – 10 % in quantity through each reactivation process, relatively more on the coal derivative and less on the petroleum derivative.

4) Estimation of Life of Activated Carbon

At the Zay water purification plant, the filtration velocity (LV) is 230 m per day (= 123,000 m^3/day ÷ 188/32 m^3 x 6 units), the space velocity (SV) is 16 from:

[= { 230 m/day (= 123,000 m^3/day/(88.32 m^3 x 6 units))

and the contact time of activated carbon is 3.75 minutes from:

(0.60 m (depth)/LV) x 60 min/hr = (0.60/(230/24)) x 60

As known from the above, the contact time is short as less than four minutes as the filtration layer is correspondingly thin. Accordingly, the space velocity, an indicator of a volume of water passing per hour against the volume of the activated carbon, is considerably high.

When intermediate chlorination is made, the life of activated carbon is said to be over at a rate of 5,000 to 8,000 times the volume of GAC. Assuming that the rate be as high as 10,000 times, the life of it would extend to approximately one month after each intermediate chlorination, as:

(52,992 m^3/unit x 6 units x 10,000) ÷ 123,000 m^3/day = 25.8

In this case, a regeneration furnace capable of six tons per day (5.3 tons as given in (2)-(e) would be necessary.

This value is assumptive, of course. A real value should be obtained by experiment.

5) Regeneration of Carbon

Actually, the activated carbon layer at the Plant is thin, so the life of the activated carbon is thought to be relatively short. In (4) above, we made a trial calculation using an assumptive lifetime of 10,000 times. However, if the actual life is 5,000 times, then a substantially large reactivation furnace capable of 10 tons per day would be necessary.

Reactivation could be made on the part of manufacturer, of course, but when transportation costs and the costs of additional activated carbon needed for a relief during reactivation are taken into account, on-site reactivation is considered appropriate.

For your information, a ten-ton reactivation furnace is given below with technical data and cost:

Model:	Multiple stage furnace
Outside Dimensions:	Approx. 3.5 m in diameter, approx. 6 m in height
Fuel:	Light Oil, 0.6 m^3/ton of GAC
Cost of Oil:	¥40,000 per ton (= 0.6 m^3/ton x ¥62,000/m^3 = ¥37,200)
Furnace Construction Cost (including boiler and other associated machines):	Approx. ¥250 million

For the operation of a reactivation furnace like this, highly technical control would be required over combustion temperature, oxygen concentration in combustion gas, etc. However, this is not so a difficult problem as a system of this type is largely automated, so that it could be operated by the local staff only upon training by manufacturer.

4-3 Reduction of THM by Blending with Available Water

The water purification system prevailing in the Amman area use raw water taken from wells and oases so that the THM formation potential in the water is extremely low. In this connection, there are two alternative methods are conceivable from a THM reduction viewpoint for future water supply, that is, whether to supply the purified Canal water to separate areas or to supply this kind of water by blending with the presently purified water.

However, the former method would inevitably be exposed to risks to be caused by the THM in the water, so, it is anticipated that the dwellers drinking this water would put out a complaint. The latter method would also be unsatisfactory but the whole population of Amman would hopefully take an equal share upon recognizing the fact that the taking of water from the East Ghor Canal is a must in view of ever increasing volumes of drinking water owing to the population increase and the improvement of the living standards in Amman.

From the above aspect, another method is also conceivable, that is to blend the water coming through the existing system from the wells and oases and the water coming from the Zay purification plant.

In this case, there would be two sites useful for blending; the terminal reservoir and the others in the Amman city area. The latter would require a less extensive alteration for blending. On the other hand, however, the terminal reservoir has a larger capacity of 250,000 m^3 in which a volume of water equivalent to two days' supply could be stored. Therefore, the amount of THM of the water in that terminal reservoir would have reach to maximum terminal state. About the water with high THM formation potential, it is considered better for supply as early as possible to decrease instantaneous THM of tap water in service area. Therefore, blending in the terminal reservoir would be better in order to decrease a retention time of water supplied from Zay plant, if practical.

Our cost estimates for blending are given below:

Case A: Blending in the Amman City reservoir, with a pipe line of 500 mm in diameter and 15 km in length laid down and flow rate control made at the inlet to the water supply plant:

Piping work:	¥ 600 million
Restructuring work:	20 million

Case B: Blending in the terminal reservoir, with a pipe line of 1,000 mm in diameter and 40 km in length laid down and a pump station installed:

Piping work:	¥4,000 million
Pump Station:	200 million

4-4 Use of Synthetic Polymer Coagulant

In the test using cationic polymer coagulant with an aim at removal of THM precursors by coagulation-sedimentation, we succeeded in obtaining a good result. We mentioned briefly about it hereunder (by Dr. Y. Magara and T. Aizawa). As for a cationic polymer coagulant, the EPA of USA permits a dose of Betz 1195 to 25 ppm.

The test result in which Betz 1195 was used in combination with alum is shown in Fig. h.

Notes: Sample water containing added kaoline was used to represent sewage water discharged after treatment. Therefore, the quality of it should differ from river water but the test result could be used to analogize effects of the cationic polymer coagulant concerned.

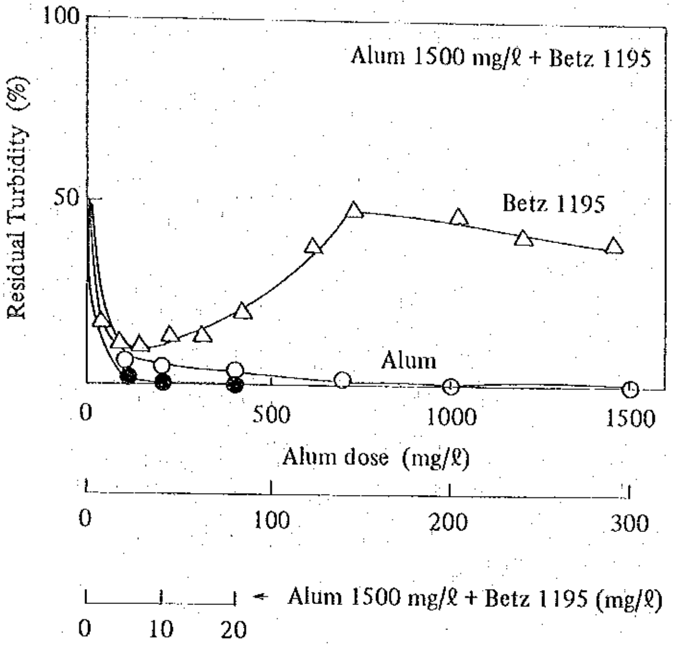


Fig. 4-8 Coagulant Dose and Residual Turbidity

Fig. 4-8 shows the removal rate of turbidity by combined use of alum and Betz 1195.

From the above figure it is known that when Betz 1195 alone is injected excessively, the flock disperses and the turbidity increases. When both alum and Betz 1195 are injected in combination after a dose of alum is set constant at 1,500 mg/ℓ while Betz is dosed at varying rates, the turbidity removal rate becomes higher than in the case of alum alone or Betz 1195 alone.

Figs. 4-9 through 4-14 show removal rates of TOC, TOXFP, THMFP, color, E260 and E220, respectively.

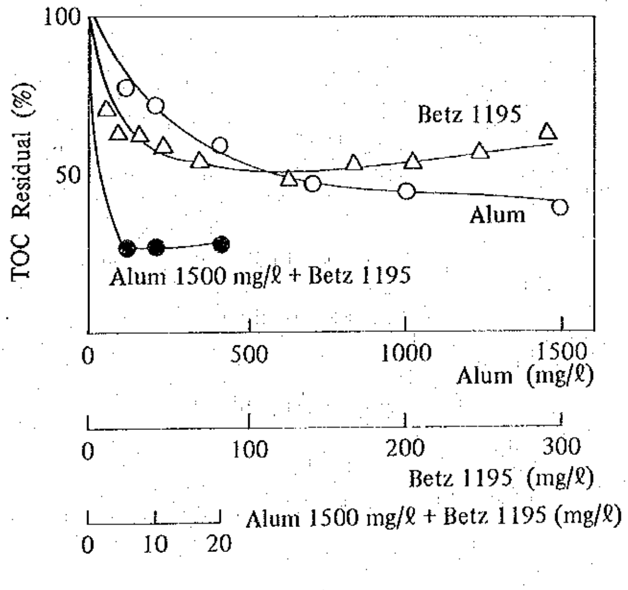


Fig. 4-9 Coagulant Dose and TOC

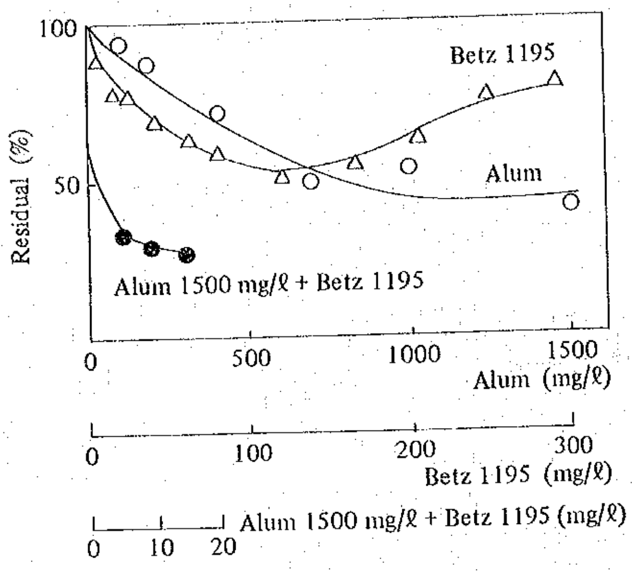


Fig. 4-10 Coagulant Dose and TOXFP

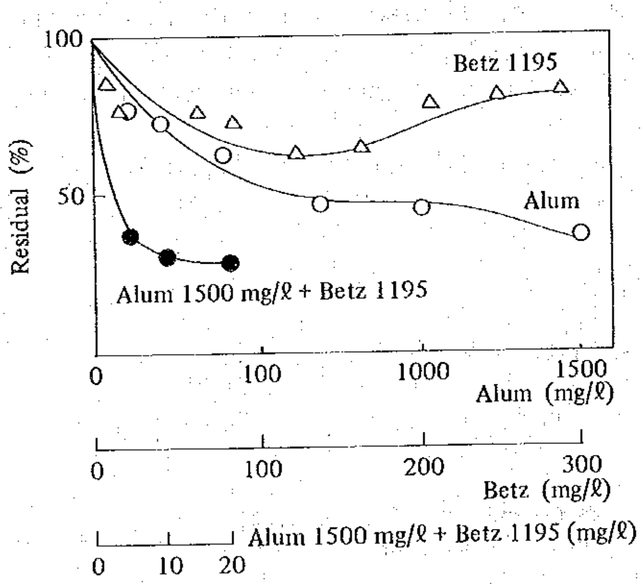


Fig. 4-11 Coagulant Dose and THMFP

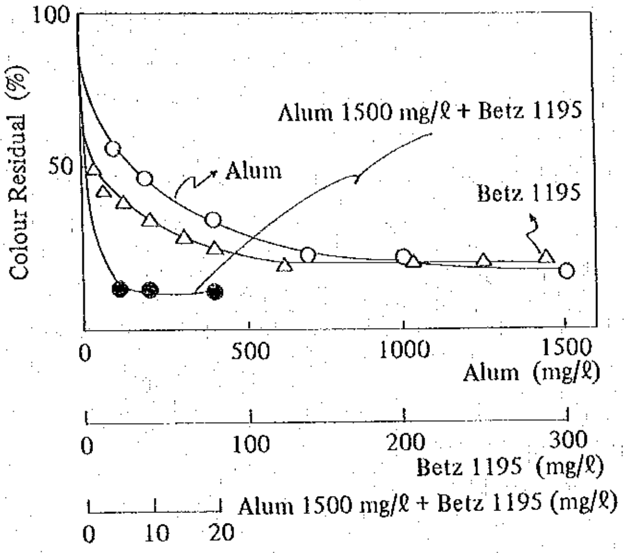


Fig. 4-12 Coagulant Dose and Colour Residual

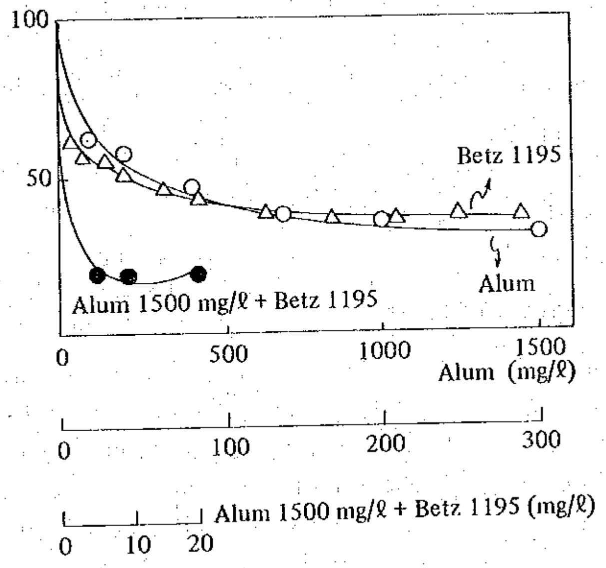


Fig. 4-13 Coagulant Dose and E_{220}

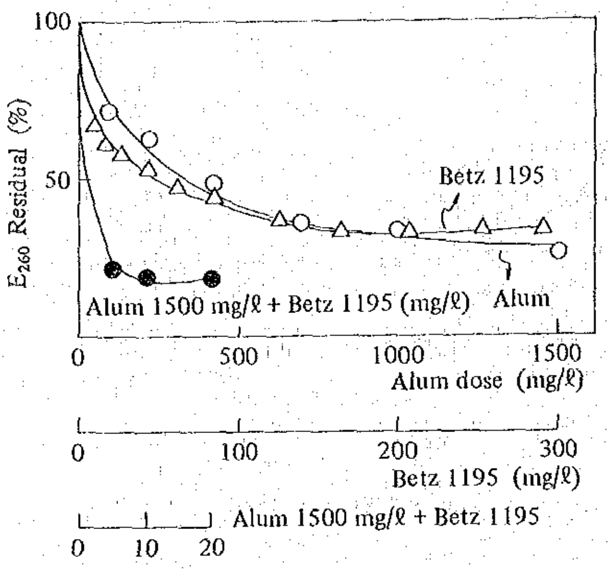


Fig. 4-14 Coagulant Dose and E_{260}

As obvious from the above figures, the tested substances are removed at almost the same rate in either case of Betz 1195 alone or alum alone. However, when Betz 1195 and alum are used combinedly, the removal rate of each substance is seen to increase. It is roughly 70 % about TOC, TOXFP or THMFP, and higher as approximately 80 to 90 % about color, E_{260} or E_{220}.

The dose of alum used in this test was so much as 1,500 mg/ℓ as against the 60 mg/ℓ dose at maximum at the Zay Plant.

It is advised in this connection that first a jar test be made by changing a coagulant dose and a synthetic polyer coagulant dose and, after confirming its effect, the use of alum be considered.

4-5 Intake from Another Point Up from Yabis

As mentioned in the section of quality analysis of water, the water taken from Deir Alla is considerably contaminated by human and agricultural activities and the total THM is expected to rise in excess of 100 μg/ℓ by normal processing. In the sections up to the previous one, we discussed various measures one by one which can be put into practice within the Zay Plant, such as the strengthening of powdered activated carbon, the introduction of low pH coagulation, the introduction of intermediate chlorination, the use of granular activated carbon and the possibility of synthetic polymer coagulant. Also, we suggested blending of the Canal water with the water from the existing well water system at supply and distribution points.

As each of the proposed measures above is necessitated from the fact that the Canal water is contaminated, and as there is no other place than the East Ghor Canal as a source of drinking water, we would be compelled to look for some other site where the quality of water is no worse than that at Deir Alla. According to the data of water quality presented by the WAJ and analyzed by us, we would choose a point around Yabis.

From the experimental data of the samples taken at Addassiyyeh and Deir Alla, we could hardly expect a substantial reduction in the total THM formation, and we would presume that water taken from anywhere along the Canal would be only slightly better than the water from Deir Alla. However, even about the Canal water, the quality of it down from Yabis would seem to variate considerably and purification of it would seem to be difficult likewise.

Accordingly, we suggest that investigations about the water quality be made at several points along the Canal and sample taken from the Yabis area be checked to determine whether it is adequate for reliable water purification toward reducing THM formation potential. But final decision should be made only after all is clarified. In this connection it is advised that an attainable economical effect be studied, for which we present below our estimation of all costs involved:

(a) Four intake pumps:

Type: Vertical, 28.3 m^3/min, 30 m head, 220 kW

Costs:	Four Pumps (60 million each)	¥240 million
	Electric Equipments	100 million
	Pump Station	60 million
	Cabling from Source, 30 km	140 million
	TOTAL	¥540 million

(b) Piping (Distance from Yabis to Deir Alla as 30 km)

- When a cast iron pipe line of 1,200 mm in diameter is laid down by excavation without timbering; inclusive of materials and work:

  ¥139 million per km x 30 km = ¥4,170 million

- When a Hume pipe (Reinforced Concrete Pipe) line of 1,200 mm in diameter is laid down:

  ¥ 89 million per km x 30 km = ¥2,670 million

(c) Total Cost

- Cast Iron Piping:

  ¥540 million + 4,170 m = 4,710 million (¥4,800 million)

- Hume Piping:

  ¥540 million + 2,670 m = 3,210 million (¥3,300 million)

Table 4-1 Cost Estimations for Recommended Measures

No.	Measure	System	Equipment	Initial Cost (x ¥10,000)	Running Cost			Annual Operating Cost (x ¥10,000) a x 123,000 x 365 ÷ 10,000	
					Chemical	Dose (mg/ℓ)	a Cost (¥/m³)		
1	Low pH Coagulation	Tank Injection	Tank, valves, frames, etc.	(850 ~ 950) + 120 ≒ 1,000	H_2SO_4	80	1.84	8,260	
		Pump Injection	Tank, pump, valves, electric equip.	1,120	H_2SO_4	80	1.84	8,260	
2	Injection of Powdered Activated Carbon (PAC)		Injection pump alteration	300	PAC	10	6	26,937	
					〃	20	12	53,874	
					〃	30	18	80,811	
3	Treatment with Granular Activated Carbon (GAC)	Life Cycle: 30 days		Total (42,380)					Life as 30 days
			Test equipment	600	Activated carbon for replenishment, (120 %)			16,536	Loss: 10 % each time
			Coal derivative GAC	13,780	Light Oil 26,496 t/U x 6 U x 12 x 0.6 kℓ/t x 62,000 ¥/kℓ			7,096	Reactivation 12 times per year
			Reactivation equipment	25,000					
			Storage tank with pipings	3,000			Total	23,632	
4	GAC	Life Cycle: 300 days		Total (22,380)					
			Reactivation Equipment	5,000					
			and others same as above	17,380	(1/10 of above)			2,363	
5	Blending with Available Purified Water	Amman City area	pipe	62,000					
		Terminal Res.	pipe + pump	420,000	Electric Charges			10,512	300 kWH x 2 x 24 x 20 x 365
6	Separate Induction		Water pump with cast iron piping	480,000	Electric Charges	(When operating in full)		15,417	220 kWH x 4 x 24 H x 20 ¥/kWH x 365
			Water pump with concrete piping	330,000	〃	〃		15,417	

4-6 Comparison of Costs

Our cost estimates are already summarized for comparison in Table 4-1. It should be noted that the given cost estimates regarding activated carbon can vary extensively by the dose of powdered activated carbon or by the life of granular activated carbon. It is seen that those which require more initial cost are the cases of blending with available purified water and of separate collection, and those which require more operating cost are the methods of using powdered activated carbon (PAC) and of using granular activated carbon (GAC). Supposing that a dose of PAC in excess of 20 mg/ℓ be made annually, the GAC treatment method would become cheaper in 2 to 3 years even though the life cycle of it is 30 days. So, we suggest that a study about initiating the GAC method be started only after such essentials are checked thoroughly about the PAC method as how long a period each year and how much PAC would have to be used.

It is known from the present series of simulation tests that the low pH coagulation method is most effective. When a view is given to the test data about the alkalinity of the Canal water which is more or less constant throughout the Canal, the dosing of sulfuric acid is necessary, even though water is taken from upstream.

Although intermediate chlorination is omitted from the Table for the reason that it involves no alteration in the existing equipment, it can be initiated at anytime and in any way.

Obviously all the cost estimates given are based on the Japanese market price. So, we recommend that you make estimates according to Jordan market conditions, while making a review over the given effects before you make final decision.

5. THM Test Method

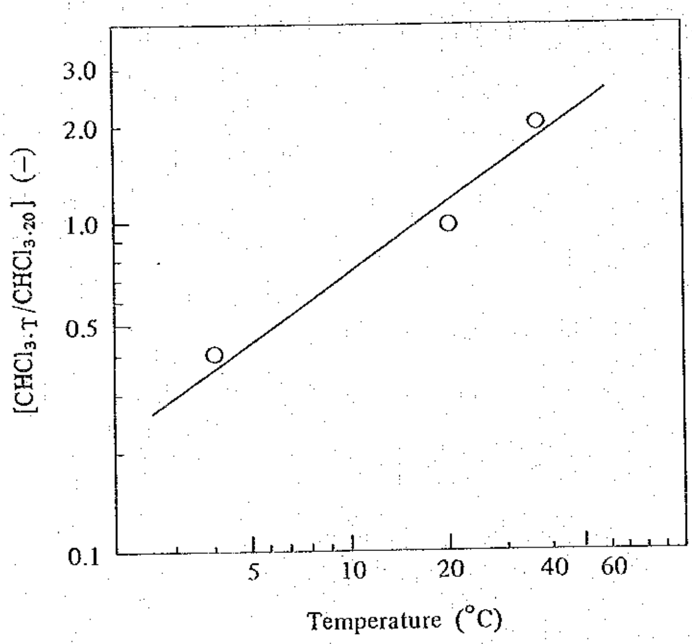
As to the measurement of THM in the tap water and in the THM formation potential, the followings should be noted for selecting a test method.

The THM formation velocity in the reaction of chlorine and precursor is normally slow. In some cases it takes more than two weeks until reaction is completed. Even when raw water is processed, the THM formation rate in the tap water varies by water temperature, pH, or the time lapse from chlorine dosing. The relation between the THM formation rate and the pH or the residual chlorine is such as mentioned already.

The water temperature has a large effect on the THM formation rate as in the case of the pH, and its relation with the 5 mg/ℓ humic acid solution is verified through test as given in Equation 5-1 and Fig. 5-1.

$$\left[\frac{CHCl_3 \cdot T}{CHCl_3 \cdot 20} \right] = 0.140\,[T]^{0.71} \quad \cdots\cdots\cdots\cdots \quad 5\text{-}1$$

$CHCl_3 \cdot T$: Chloroform formation rate (μg/ℓ) at reaction temperature
$CHCl_3 \cdot 20$: Chloroform formation rate (μg/ℓ) at 20°C. reaction temperature
T : Temperature (°C.)



(Condition: Chlorine dose 10 mg/ℓ, humic acid 5 mg/ℓ, reaction time 1 day and pH 7.0)

Fig. 5-1 Relation between Chloroform Formation Rate and Reaction Temperature

The tap water and the test sample of THM formation potential subjected to measurement are normally in the middle of reaction. Accordingly, included in the sample water are (1) THM which have been formed already (2) THM intermediate which is going to change to THM by hydrolysis consequent to affixation of chlorine to precursor and (3) residual chlorine and precursor which has not reacted yet. As regards the test sample involved, that which is subjected to measurement is only the THM which has formed already. Therefore, it would be impossible to measure a correct amount of THM unless prevention of THM intermediate from hydrolyzing and of reaction between chlorine and prescursor should be effectively made, otherwise, variation in the analysis would become extensive. The above is the reason that differs much from the measurement of such low boiling point organic chlorine compounds as trichloroethyleene, and tetrachloroethylene.

For preventing THM intermediate from hydrolyzing and the rection between residual chlorine and precursor in the analysis process, the Japanese official trihalomethane analytical method provides a measuring method for the formed THM only after such pre-treatments as (1) add sodium sulfate or sodium thiosulfate in stoichiometric excess of the quantity which reacts to residual chlorine for stopping the reaction of the precursor to the residual chlorine and (2) Add phosphoric acid or sulfuric acid to adjust the pH to approximately 2 and then make a necessary treatment. . . . . . Further, when it takes a long time from sample collection to THM measurement, it is necessary to remove chlorine immediately after sample is collected to adjust the pH of the sample to 2, and it is desired to transport and store it after the sample is cooled to below 5°C.

Next, we describe characteristics including some disadvantages of the following analysis methods: (1) The Japanese head space analysis method (2) Japanese solvent extraction method (3) US purge trap method and (4) Jordan head space method.

5-1 Head Space Method (Japan)

1) Sampling

(1) Date of sampling

Samples shall be collected in the same day, as a rule, in the system of the same water purification plant; providing that when collecting in the same day is very difficult, samples may be collected in days as close as possible in the same system.

(2) Sampling method

1 Samples shall be collected from a tap (the water supply site for drinking water by a bulk water supply body).

2 For collecting water samples, the tap is opened for a while to flow the stagnant water out and after the water temperature becomes constant, a sample is collected.

3 Add an adequate amount of sodium thiosulfate solution (0.5 w/v %) in a glass bottle which has been well rinsed by deionized water to remove remaining chlorine. Put a sample into the bottle quietly so as not to bubble, and add phosphoric acid (1 + 10) or sulfuric acid (1 + 5), with a rate of approximately a drop per 10 mℓ to adjust pH at about 2. Then the bottle is filled with water and sealed with a stopper.

(3) Transportation of sample

1 Cool the sample with ice, transport and test it quickly.

2 When there is a risk of contamination of the sample during transportation, transport control water containing n-trihalomethane by the same method added to the sample to confirm the presence or absence of contamination. When entrusting the test of the sample to the outside facility, this shall be particularly noted.

2) Analytical Method of Total Trihalomethane

(1) Reagents*1

1 Deionized water

For obtaining distilled water, put 2 liters of ion-exchanged water into a separating funnel, and add 100 mℓ of n-hexane for a residual pesticides analysis grade; after shaking, remove the n-hexane layer. Put the aqueous layer into an Erlenmyer's flask and after boiling to remove n-hexane, put into a distilling flask and distil twice. The distilled water is boiled for 20 minutes and cooled before using each time.

The deionized water is preserved in a place free from contamination with trihalomethane.

2 Methanol for residual pesticides analysis grade

The methanol shall not have the peak near an expected retaining time of trihalomethane in gaschromatography.

3 Sodium thiosulfate solution (0.5 w/v %)

Dissolve 0.5 grams of sodium thiosulfate in deionized water to make up to 100 mℓ.

4 Phosphoric acid (1 + 10)

Mix 10 mℓ of phosphoric acid with 100 mℓ of deionized water.

5 Trihalomethane standard stock solution

Solve 0.200 grams of chloroform, 0.100 grams of bromodichloromethane, 0.400 grams of dibromochloromethane, and 2.000 grams of bromoform in methanol and mix and make up to 100 mℓ.

One milliliter of the solution contains 2 mg of chloroform, 1 mg of bromodichloromethane, 4 mg of dibromochloromethane and 20 mg of bromoform.

The solution shall be preserved in a cold place.

6 Trihalomethane standard solution

Dilute the trihalomethane standard stock solution with the methanol stepwise to 5 to 200 fold.

One milliliter of the solution contains 0.01 – 0.4 mg of chloroform, 0.005 – 0.2 mg of bromodichloromethane, 0.02 – 0.8 mg of dibromochloromethane, and 0.1 – 4 mg of bromoform.

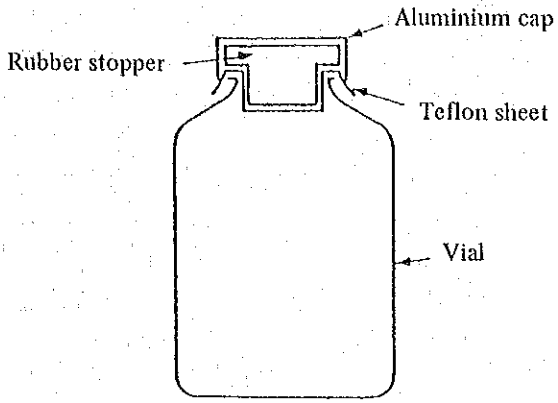
The solution shall be prepared before each use.

Note *1) The reagents used in the test are of the special grade of JIS (Japan Industrial Standard) unless otherwise specified.

(2) Devices and apparatuses

1 Vial:

A 10 – 200 mℓ vial for injection[*2], as roughly shown in the figure:



2 Rubber stopper for vial:

A rubber stopper which can be tightly attached to the vial, as roughly shown in the figure.

3 Teflon sheet:

A teflon sheet of 0.05 mm thick which is large enough to separate the sample water from the stopper when inserting it between the rubber stopper and the vial.

4 Aluminium cap:

Aluminium cap which can fasten the vial and the rubber stopper for vial, as roughly shown in the figure.

5 Aluminium cap clamp:

Aluminium cap clamp for clamping the aluminium cap to the vial to fix it.

6 Thermostat water bath:

A thermostat which can keep the temperature at 20 ± 0.2°C.

7 Microsyringe (for fluid):

A microsyringe which can draw in 1 to 10 μℓ.

8 Microsyringe (for gas):

A microsyringe which is air gas tight and can draw in 50 – 1000 μℓ.

9 Gaschromatograph:

A gaschromatograph which is, as a rule, shown below.

a) Column:

A glass tube of 3 mm inner diameter and 3 meter length, the temperature of which is 60 – 100°C.

b) Column packing:

A substance prepared by coating Chromosolb W (particle size, 177 – 250 nm) which is rinsed by acid and treated with silane or a carrier which has properties the same as or higher than those of Chromosolb by 10 – 20 % with Silicon DC-200, Silicon DC-550 or a fluid which has a separating capacity the same as or higher than that of Silicon DC-200 or DC-550.

Note *2) In a series of an analytical system, vials of a given size shall be used.

c) Detector:
A detector of an electron capture type, the temperature of which is 200 – 250°C.

d) Sample inlet:
A sample inlet kept at 200 – 250°C.

e) Carrier gas:
Nitrogen or helium of 99.999 v/v % or more with a flow rate of 60 – 80 mℓ/m.

(3) Testing operation

1 Pretreatment

Take test water in a vial to obtain the quantity of a test sample/vial volume = 0.70 – 0.85*3, and put the rubber stopper for the vial while inserting teflon sheet immediately; put aluminium cap on the stopper and fix the rubber stopper to the vial by the aluminium cap clamp. Inject the methanol by the microsyringe for fluid with a rate of 1 μℓ of the methanol per 100 mℓ of the test sample water. After vigorously shaking the vial, put the vial up side down and leave in a thermostat at 20 ± 0.2°C for 1 hour; the obtained solution is used as a test sample.

2 Analysis

Take a given amount of the test sample in a gas phase obtained in the above process the 1) by a microsyringe for gas through the rubber stopper for the vial, immediately introduce into a gaschromatograph to record the gaschromatogram. Measure the height of the peak which is corresponding to the retention time of trihalomethane, obtain the contents of chloroform, bromodichloromethane, dibromochloromethane and bromoform in the test solution from the calibration curve prepared by (4), and calculate each concentration in the test water.

Sum up these concentrations to obtain the total trihalomethane in the test water.

(4) Preparation of calibration curve

Take purified water as described 1) in (3), and fix with the aluminium cap clamp; inject the trihalomethane standard solution, which is prepared stepwise, through the rubber stopper for the vial with a rate of 1 μℓ per 10 mℓ of purified water by a microsyringe for fluid. Then, treat as described in 1) and 2) in (3) to obtain the relation between the contents of chloroform, bromodichloromethane, dibromochloromethane, and bromoform and the heights of their peaks.

3) Characteristics of Head Space Method (Japan)

(1) No reaction occurs of precursor to residual chlorine

(2) No hydrolysis occurs of THM intermediate

(3) As the partition coefficient to gas phase and liquid phase would change when the ion strength in the sample is large, it would be necessary to adjust the ion strength of the standard solution to match the ion strength of the sample. This could be attained by adding sodium chloride at a rate of 10 % to each of the standard solution and the sample, whereby the sensitivity of the method would be double. However, there should be no effect of ion strength on an sample which has an electric conductivity at less than 500 μS/cm.

Note *3) In a series of an analytical system, a given rate shall be used.

(4) The detection limit of chloroform, bromodichloromethane or dibromochloromethane is higher than 0.5 μg/ℓ while that of bromoform is at 2 μg/ℓ or less. Therefore, bromoform is not suitable for sample of low concentration.
(5) Easy to operate with no solvent needed in the analysis.
(6) Caution must be taken against contamination from ambient air in where the analysis is taking place however.
(7) Less contamination of electron capture detector.
(8) No special equipment is necessary.
(9) Continuous measurement by gas chromatograph is possible.

5-2 Solvent Extraction Method (Japan)

1) Sampling

The same as in 3-1-1.

2) Analytical Method of Trihalomethane

(1) Principle

This method extracts a low boiling point organic halogen compound by n-hexane (or n-pentane) from the sample water and measures the extraction by means of gas chromatograph and finally obtain a concentration of the low boiling point organic halogen compound.

(2) Reagent

1) Purified Water:
Take two liters of distilled water or ion exchanged water into a separating funnel and, after adding 100 mℓ of n-hexane of residual pesticide testing grade, shake it vigorously. Then, transfer the aqueous layer of it into an Erlenmyer's flask and boil it to remove the n-hexane from it. Thereafter, transfer it into a distilling flask and distill it twice. This purified water should be boiled for ten minutes and cooled down before being put to use. Also, this should be stored where there is no danger of contamination by the low boiling point organic halogen compound.

2) n-hexane:
Condense 100 mℓ of n-hexane to approximately 1 – 5 mℓ. Take 5 μℓ out of it and put it into a gas chromatograph, with no peak generating in the neighborhood of the expected retention time of the object substance. n-pentane may be used as a substitute.

3) Methyl Alcohol:
Condense 100 mℓ of methyl alcohol to approximately 1 – 5 mℓ. Take 5 μℓ out of it and put it into a gas chromatograph, with no peak generating in the neighborhood of the expected retention time of the object substance.

4) Sodium Sulfate Solution (0.5 w/v %):
Dissolve 0.5 g of sodium sulfate in purified water to obtain a 100 mℓ solution. This solution should be adjusted everytime it is put to use.

5) Phosphoric Acid (1 + 10)

6) Sulfuric Acid (1 + 5)

7) Standard Solution of Low Boiling Point Organic Halogen Compound:

Put 90 mℓ of n-hexane into a measuring flask of 100 mℓ capacity. To this, add 1,000 g of chloroform, 0.250 g of bromodichloromethane, 0.4 g of dibromochloromethane, 2 g of bromoform, 1.5 g of trichloroethylene, 0.4 g of tetrachloroethylene, 0.4 g of 1,1,1-trichloroethane, 0.8 g of carbon tetrachloride and 0.25 g of chloropicrin. After dissolution of these substances, further add n-hexane to make the total volume 100 mℓ. 1 mℓ of this solution contains 10 mg of chloroform, 2.5 mg of bromodichloromethane, 4 mg of dibromochloromethane, 20 mg of bromoform, 15 mg of trichloroethylene, 4 mg of tetrachloroethylene, 4 mg of 1,1,1-trichloroethane, 0.8 mg of carbon tetrachloride and 2.5 mg of chloropicrin. The mixing ratio of these substances is set for the purpose that all the substances should rise to peak heights at nearly the same level in the gas chromatograph in case DC-550 is used for filling the column. Therefore, when a different filler is used, this ratio should be adjusted appropriately.

(3) Implements and Equipments

1) Measuring cylinder with a stopper of 50 mℓ capacity

2) Microsyringe of 1 – 10 μℓ liquid capacity

3) Gas chromatograph:

a) with sample inlet temperature set to 150 – 250°C.

b) with a glass column of 3 mm inside diameter and 3 m long with its temperature set to 60 – 100°C.

c) with column (Note 1) of silane treated chromosorb W (grain size: 177 to 250 um) after acid rinse or a carrier having an equal or better function which is masked by 20 % silicon DC-550 or 20 % silicon DC-200 or by a liquid phase having an equal or better separating capacity.

d) with a detector of electron capture type with a temperature set to 150 – 250°C.

e) with carrier gas as nitrogen gas of a purity higher than 99.999 v/v % with its flow rate regulated to 40 – 80 mℓ per minute.

Note 1. When the gas chromatographic analysis is made using only one kind of column it is difficult to thoroughly separate every standard substance. For this reason, more than two kinds of columns with different separating properties should be used in columns. By this way, gas chromatograms are recorded and quantitative analysis is made by using non-overlap peaks. If anyone of the column mentioned above is found not satisfactory with respect to its separating capacity, any of such ones could be used instead as: 20 % silicon SF-96, 3 % silicon SE-52, 10 % FFAP, 20 % TCP, 20 % PEG20M, and 20 % DC-550 + 20 % SF-96 (2 + 8).

(4) Test Procedure

1) Pretreatment:

Take 40 mℓ of test water into a measuring cylinder and add 10 mℓ of n-hexane and tightly plug it. Then, vigorously shake it for 10 to 20 seconds and place it still. The n-hexane layer is the test liquid.

2) Analysis:

After the above pretreatment, take a dose from the test liquid by microsyringe and immediately inject it into the gas chromatograph. Then take a record of the gas chromatogram. About the peak not overlapping any other compound, obtain a peak height or a peak area equivalent to the retention time of low boiling point organic halogen compound.

Note: In case n-pentane is used instead of n-hexane, the microsyringe should be cooled by ice in advance.

3) Preparation of Calibration Curve:

Take a dose from the standard solution of low boiling point organic halogen compound which has been prepared step by step, and by the same procedure as in 2) above, obtain the relation of the quantity of each component (ng) of the low boiling point organic halogen compound with its peak height or peak area.

4) Calculation of Concentration:

From the peak height or the peak area obtained in (2) above, obtain a quantity (a ng) of each component of the low boiling point organic halogen compound in reference to the calibration curve in (3). Then, calculate the quantity within 1 liter sample by the following equation:

$$\frac{a}{\text{Dose }(\mu\ell)} \times \frac{\text{Test Liquid Volume }(\text{m}\ell)}{\text{Test Water Volume }(\text{m}\ell)} \times 1000$$

Test liquid volume: Extracted solvent volume

Note 1. According to the standard for reagents, it is specified to use the standard reagent for trihalomethane analysis use, the reagent for low boiling point organic halogen compound analysis use or any other which is equal to or better than any of the standard reagents.

Note 2. The limit of detection on the low boiling point organic halogen compound in respect of this analysis method varies by factors such as the type of gas chromatograph used and the measuring condition. However, it is desirable that the limit of detection be set to a level of 0.001 mg/ℓ and the detector be well taken care of through maintenance and control.

3) **Characteristics of Solvent Extraction Method**

(1) No interaction occurs between precursor and residual chlorine.

(2) No hydrolysis occurs of THM intermediate.

(3) The ion strength of sample has no effect upon analysis of THM.

(4) Easy to operate but a solvent of high purity is needed, however.

(5) No special equipment is needed.

(6) Contamination of the electron capture detector is larger in this method than in the head space method.

(7) Continuous measurement is possible by gas chromatograph.

(8) Although the detection limit of chloroform is inferior, than those dibromochloromethane or bromoform.

(9) As n-hexane used as extraction solvent may be obstructed by a negative peak of the solvent immediately before chloroform reaches its peak. For this reason, careful selection should be made of an adequate column. n-pentane may be used instead, but the negative peak which it will generate will never obstruct the measurement of chloroform. But, as the boiling point of n-pentane is as low as 36°C., it would be inadequate for use in an enclosed working environment.

5-3 Purge Trap Method (U.S.A.)

1) Introduction of Purge Trap Method

HALOGENATED METHANES AND ETHANES BY PURGE AND TRAP*

Organohalides, particularly the trihalomethanes, have been reported in nearly every chlorinated water supply tested in the United States.[1] Common organohalide solvents, traceable to industrial effluents, have been detected in many raw source waters and in the corresponding finished drinking waters, but they are most often the result of chlorination. Toxicological studies suggest that chloroform ($CHCl_3$) and other organohalides have had detrimental effects on human health. Their presence in water supplies should be monitored closely so that measures may be taken to minimize or eliminate them whenever concentrations approach levels of concern.

(1) General Discussion

a. Principle: This method is applicable to the determination of the following organohalides contained in water: all chloromethanes, chloroethanes, and chloroethylenes, bromomethane, dibromomethane, bromochloromethane, bromodichloromethane, chlorodibromomethane, bromoform, and 1, 2-dibromoethane. Other organohalides that boil at less than 150°C and that are less than 2% soluble in water are determined also. However, the analyst must demonstrate the usefulness of the method by collecting accuracy and precision data using dosed and actual samples.

An inert gas is bubbled through the sample to transfer the volatile constituents from the aqueous phase into the purge gas. The organics contained in the purge gas are then trapped in a short column (trap) containing a suitable sorbent (Figure 53:1). After purging is complete, the compounds are desorbed thermally from the trap and backflushed (Figure 53:2) into a temperature-programmed gas chromatographic column for separation and analysis (Figure 53:3). Detection is by use of a halogen-specific detector, and for this analysis, either a microcoulometric or an electrolytic conductivity detector operated in the specific halogen mode is acceptable.

b. Interferences: Impurities contained in the purge gas and organic compounds outgassing from the system ahead of the trap usually account for most contamination problems. Such compounds will be concentrated in the trap and ultimately analyzed with the sample components. The analysis of blank samples (organic-free water) is a convenient means of monitoring for this problem. Whenever potential interferences are noted in blank samples, change the purge gas source and replace the molecular sieve gas filter (see ¶ (2) h). Outgassing from the system generally cures itself with time. Do not subtract blank values.

---

* Approved by Standard Methods Committee, 1985.

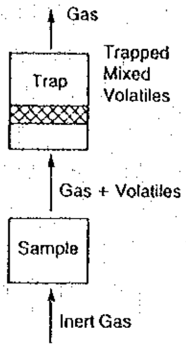


Figure 53:1. Removal of volatiles from the sample

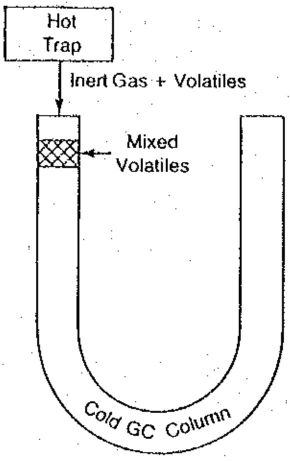


Figure 53:2. Transfer of trapped volatiles to chromatographic column

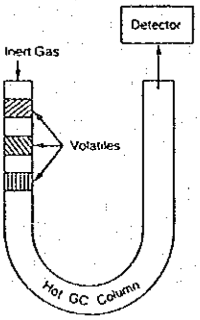


Figure 53:3. Separation of the volatiles

c. Detection limits: The detection limits are determined by the halogen-specific gas chromatographic detector selected for the analysis, the degree of halogen substitution, and the specific halogen species contained in the compound. Most of the above organohalides can be analyzed over a concentration range of approximately 0.5 to 1500 μg/ℓ.

(2) Apparatus†

Wash sample bottles and seals in detergent solution, rinse with distilled water, let air-dry, then heat to 105°C for 1 h. Once bottles and seals are cool, seal bottles using same septa intended for sample. Use more vigorous heat treatment of glassware (such as heating to 400°C in a muffle furnace) when high-boiling organic materials present contamination problems.

a. Sample bottles and seals, 40-mℓ screw-cap vials‡ sealed with TFE§-faced compressible silicone rubber septa.||

b. Microsyringes, 10-, 25-, 100-μℓ.

c. Syringe needle, 20-cm x 20 gauge.

d. Syringe, 5-mℓ valved gastight with 5-cm needle.

e. Syringe, 5-mℓ hypodermic with luerlok tip.

f. Syringe valve, two-way with luer ends.

g. Volumetric flasks, 10-, 100-mℓ.

† Gas chromatographic methods are extremely sensitive to differences in materials used. Mention of specific products by "Standard Methods" does not preclude the use of other existing or as-yet-undeveloped products that give demonstrably equivalent results.

‡ Pierce No. 13075 or equivalent. Crimp-top serum vials also are acceptable.

§ Teflon or equivalent.

|| Pierce No. 12722 or equivalent.

h. Purge-gas scrubber filter containing about 225 g granular molecular sieve.#

i. Purge and trap equipment: The purge and trap equipment consists of three separate parts, the purging device, trap, and desorber.

A successfully used[2] purging device is shown in Figure 53:4. The glass frit installed at base of sample chamber allows finely divided gas bubbles to pass through sample while it is retained above the frit. Gas volumes above the sample are kept to a minimum to eliminate dead-volume effects, yet allow sufficient space for most foams to disperse. Inlet and exit ports are constructed of heavy-walled 6.4-mm OD glass tubing so that leak-free removable connections can be made using "finger-tight" compression fittings containing TFE§ ferrules. The removable foam trap controls excessive foaming. Any similar device with a configuration such that a purge gas flow of 20 mℓ/min quantitatively (> 90 %) will strip $CHCl_3$ from solution in approximately 10 min should be acceptable.

Examples of traps and desorbers are shown in Figures 53:5 to 10. A trap is a short gas chromatographic column that at 22°C retards flow of compounds of interest while venting purge gas and, depending on sorbent used, much of the water vapor. Use a trap with a low thermal mass so that it can be heated rapidly for efficient desorption, then cooled rapidly to room temperature for reuse. The Tenax™ **-silica gel trap utilizes the sorptive properties of two sorbents, providing a trap that effectively sorbs and desorbs a wide variety of organic compounds.

A desorber is essentially a heated tube into which the trap is placed and maintained at the desorb temperature (Figures 53:6 and 7) or is heated rapidly in the desorb mode (Figure 53:9), depending on the type of purge-trap-desorb apparatus. Using this device, the trap is heated rapidly to the desorb temperature (180°C, < 0.75 min) and maintained at that temperature with minimal temperature overshoot. Trapped compounds are released as a plug to the gas chromatograph by this heat and backflush step.

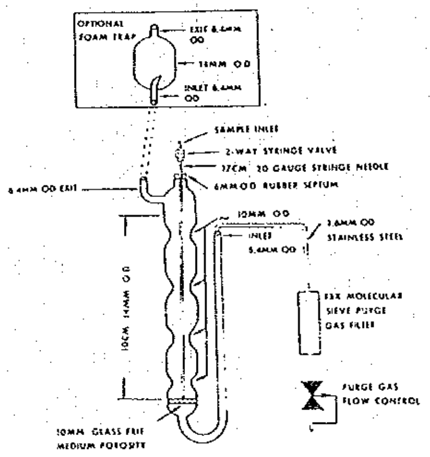


Figure 53:4. Purging device

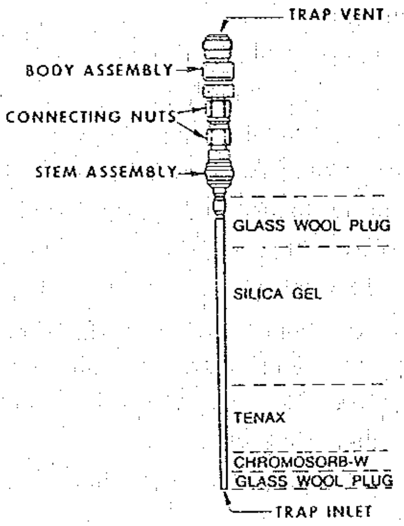


Figure 53:5. Trap

Molecular Sieve 5-A, Applied Science Laboratories, P.O. Box 440, State College, Pa., or equivalent.

** A source of this material is Applied Science Laboratories, P.O. Box 440, State College, Pa. 16801.

The trap illustrated in Figure 53:5 and two associated alternative desorbers in Figures 53:6 and 7 are easy to assemble and are relatively inexpensive, but they require considerable manipulation during analysis.

A more complex and expensive-to-build purge-trap-desorb system is shown in the purge-sorb mode in Figure 53:8 and the desorb mode in Figure 53:9. This system is easier to operate reproducibly because all manipulations requiring manual transfers of trap to purge device, trap to desorber, etc., in the first system (Figures 53:5 to 7) are accomplished by switching a single six-port valve (Figures 53:8 and 9).

The purge-trap-desorb apparatus used need not conform necessarily to the exact configurations shown so long as it functions to purge and trap the compounds of interest quantitatively or in a way linearly related to concentration. The apparatus must quantitatively desorb sorbed organics to the chromatographic column sufficiently quickly that they are deposited as a narrow band. Rapid desorption is necessary to produce good chromatographic resolution.

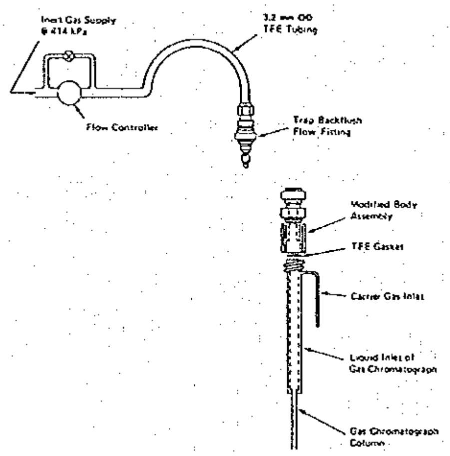


Figure 53:6. Optional desorber No. 1

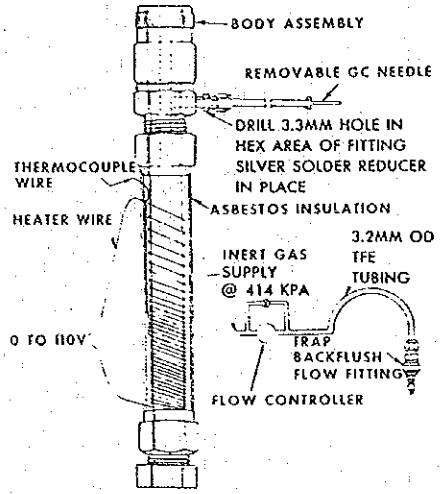


Figure 53:7. Optional desorber No. 2

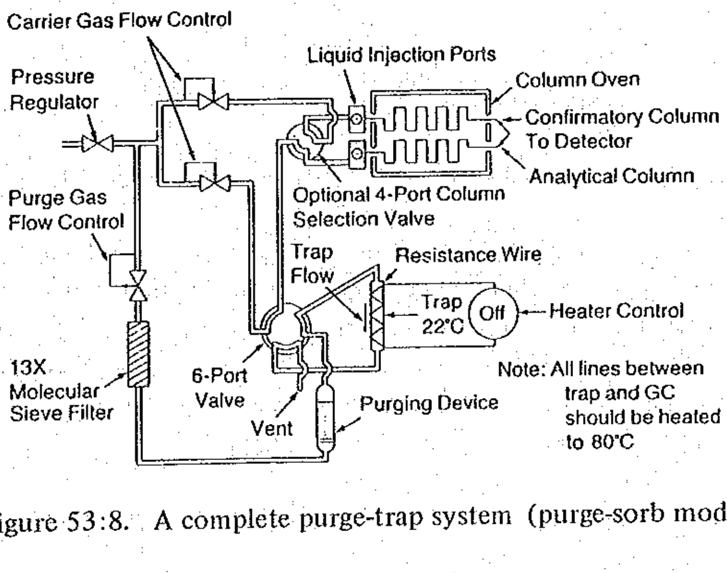


Figure 53:8. A complete purge-trap system (purge-sorb mode)

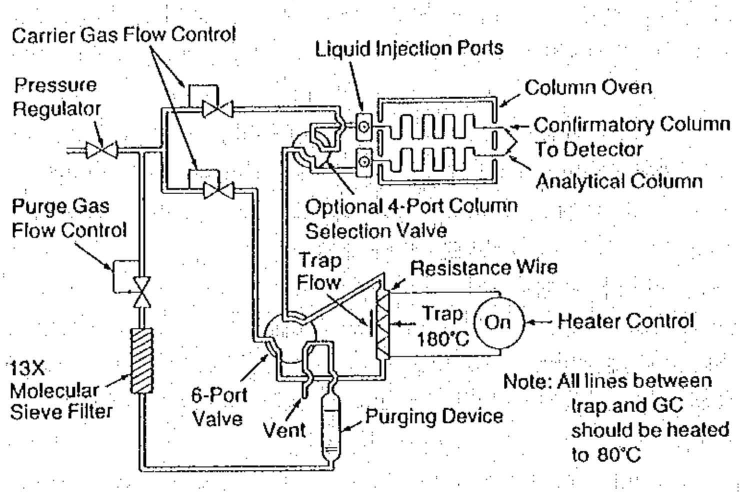


Figure 53:9. A complete purge-trap system (desorb mode)

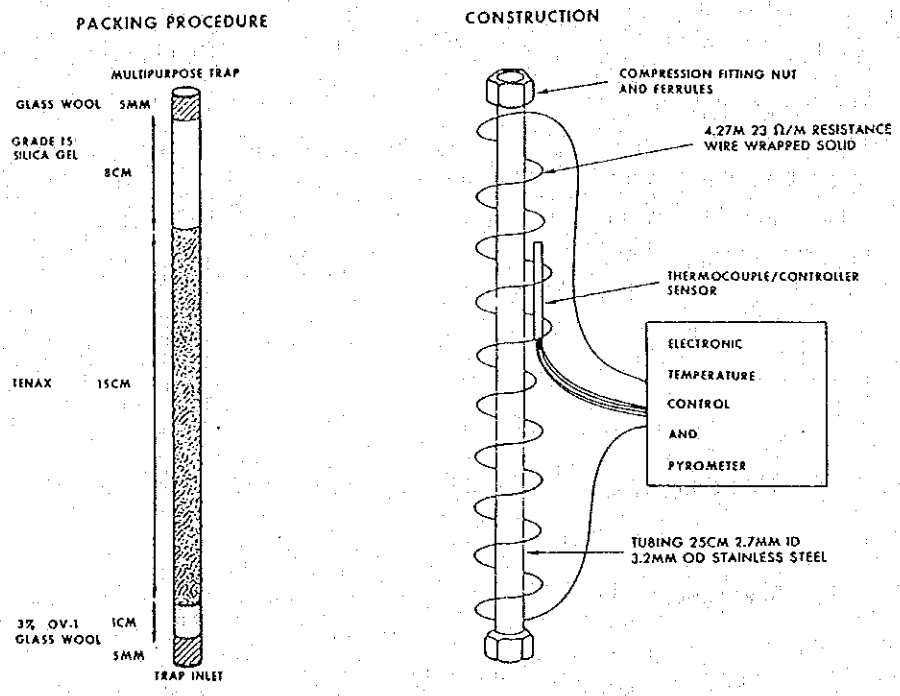


Figure 53:10. Trap and desorber for complete purge-trap system

To prepare trap (Figure 53:10), pack a 25-cm-long, 2.7-mm-ID x 3.2-mm-OD stainless steel tube as follows: Place a 5-mm plug of glass wool in inlet end of trap. Add 1 cm of 3 % OV-1 on Chromosorb-W^{TM}†† (60/80 mesh), 15 cm of Tenax^{TM}†† GC (60/80 mesh), 8 cm of Grade 15 silica gel†† (35/60 mesh), and a 5-mm plug of glass wool at exit end of trap. Variations in critical trap parameters (ID, length, sorbant type, amount of sorbent, and sorbent packing order) will affect adversely trap/desorb efficiencies.

†† A source of this material is Applied Science Laboratories, P.O. Box 440, State College, Pa. 16801.

j. Gas chromatograph, equipped with:

1) Temperature-programmable oven.

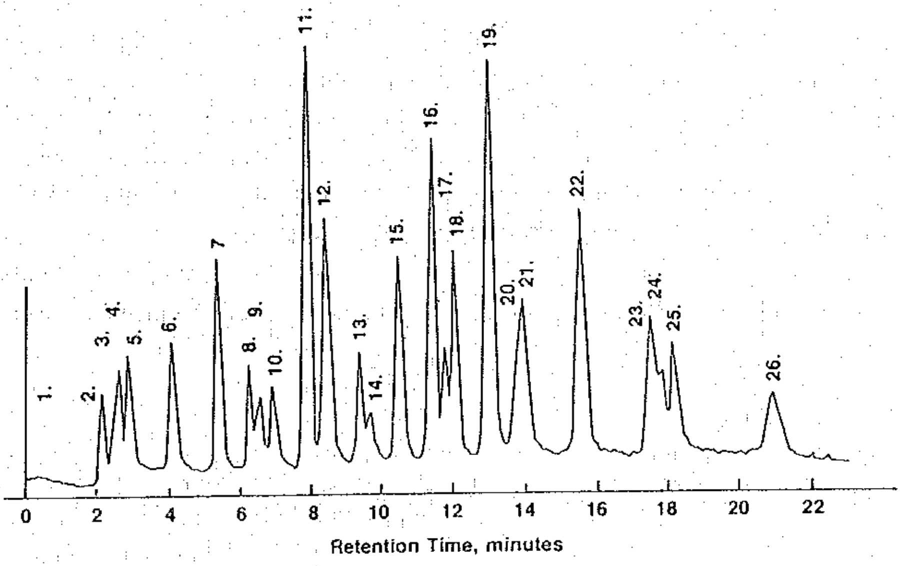
2) Injection port converted into a desorbing device (Figure 53:6[3]) for use with trap if an external desorbing device (Figure 53:7, 8, or 9) is not used.

3) Fittings for 3.2-mm columns.

4) Halogen-specific detector, electrolytic conductivity (halide mode) or microcoulometric titration (halide mode). The electron capture detector usually is too sensitive but is acceptable if satisfactory results can be demonstrated.

k. Gas chromatographic columns:

1) Analytical column – 8 ft long, 0.1 in. ID by 0.124 in. OD (or closest available metric equivalents), stainless steel or equivalent glass, packed as in ¶ (3) a. Use helium as carrier gas at flow rate of 40 mℓ/min. Program temperature as follows: With column at room temperature desorb sample into column for 4.0 min, rapidly heat column to 60°C for 3.0 min, then raise temperature 8°C/min to 160°C. Hold at 160°C until all compounds have been eluted. A sample chromatogram obtained with this column is shown in Figure 53:11.



Column: 0.2% Carbowax 1500 on Carbopack-C
Program: 60°C-3 min 8°/min to 160°C
Detector: Electrolytic conductivity

1. Inject
2. Chloromethane
3. Bromomethane
4. Vinyl Chloride
5. Chloroethane
6. Methylene Chloride
7. 1,1-Dichloroethylene
8. Bromochloromethane
9. 1,1-Dichloroethane
10. trans-1,2-Dichloroethylene
11. Chloroform
12. 1,2-Dichloroethane
13. 1,1,1-Trichloroethane
14. Carbon Tetrachloride
15. Bromodichloromethane
16. 1,2-Dichloropropane + 2,3-Dichloropropene
17. trans-1,3-Dichloropropene
18. 1,1,2-Trichloroethane
19. 1,1,2-Trichloroethane + Chlorodieromomethane + cis-1,3-Dichloropropene
20. 1,2-Dibromoethane
21. 2-Bromo-1-Chloropropane
22. Bromoform + 1,1,1,2-Tetrachloroethane
23. 1,1,2,2-Tetrachloroethylene
24. 1,1,2,2-Tetrachloroethane
25. 1,4-Dichlorobutane
26. Chlorobenzene

Figure 53:11. Chromatogram of organohalides – analytical column

2) Confirmatory column – 6 ft long, 0.1 in. ID by 0.125 in. OD (or closest available metric equivalents), stainless steel, packed as in ¶ (3) b. Use helium at flow rate of 40 mℓ/min. Program temperature as follows: With column at room temperature desorb sample for 4.0 min, heat column to 50°C for 3.0 min, then program at 6°C/min to 170°C. Hold at 170°C until all compounds have been eluted. A sample chromatogram obtained with this column is shown in Figure 53:12.

Column: n-Octane on Porasil-C
Program: 50°C-3 min 6°/min to 170°C
Detector: Electronic conductivity

1. Vinyl Chloride & Chloromethane
2. Bromomethane
3. 1,1-Dichloroethylene
4. Chloroethane
5. trans-1,2-Dichloroethylene
6. Methylene Chloride
7. Carbon Tetrachloride
8. Chloroform + cis-1,2-Dichloroethane +
9. 1,1-Dichloroethane + Bromochloromethane
10. 1,1,1-Trichloroethane + 1,1,2-Trichloroethylene
11. Bromodichloromethane
12. Dibromomethane + Tetrachloroethylene
13. 1,2-Dichloroethane
14. Dibromochloromethane + trans-1,3-Dichloropropene + 1,2-Dichloropropane
15. cis-1,3-Dichloropropene + 1,1,2-Trichloroethane
16. 2-Bromo-1-Chloropropane Chlorobenzene 1,2-Dibromoethane
17. Bromoform
18. Chlorohexene
19. Chlorohexane
20. 1,1,2,2-Tetrachloroethane + Pentachloroethane o-Chlorotoluene
21. m-Dichlorobenzene + Hexachloroethane + p-Dichlorobenzene
22. 1,4-Dichlorobutane + o-Dichlorobenzene
23. Hexachlorobutadiene
24. 1,2,4-Trichlorobenzene

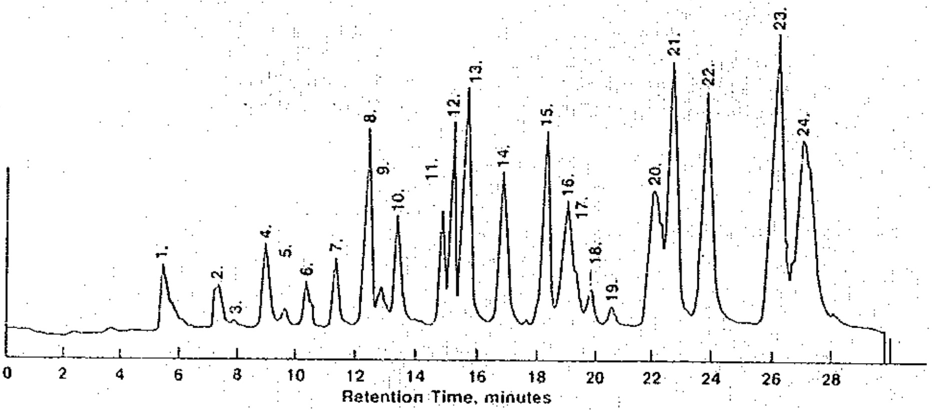


Figure 53:12. Chromatogram of organohalides – confirmatory column

(3) Reagents‡‡

a. 0.2 % Carbowax™ 1500 on Carbopack™-C (80/100 mesh).§§

b. n-Octane/Porasil™-C (100/120 mesh).‖‖

c. Three percent OV-1 on Chromosorb™-W (60/80 mesh).

d. Tenax™ GC (60/80 mesh).##

e. Silica gel Grade 15 (35/60 mesh).

f. Reference standards: Whenever possible obtain pre-analyzed reagents with guaranteed purities higher than 95 %.

g. Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$.

h. Methyl alcohol.

i. Purgeable-organic-free water: Boil distilled or deionized water for 15 min, then maintain at 90°C while bubbling contaminant-free inert gas through water for 1 h. While water is still hot, transfer to narrow-mouth screw-cap bottle with TFE seal. Test purgeable-organic-free water daily by analyzing according to this method. Do not use if significant interfering peaks are observed.

j. Standard stock solutions of compounds boiling above room temperature: Place about 9.8 mℓ methyl alcohol in a ground-glass-stoppered 10.0-mℓ volumetric flask. Let flask stand unstoppered about 10 min or until all alcohol-wetted surfaces have dried. Weigh to nearest 0.1 mg. Using a 100-$\mu\ell$ syringe, add 4 drops of reference standard to flask and reweigh. Be sure that the 4 drops fall directly into the alcohol without contacting flask neck. Dilute to volume with methyl alcohol, re-stopper, and mix by inverting flask several times. Calculate concentration in micrograms per microliter from the net gain in weight. Store at 4°C. Such standards are stable up to 4 weeks.

k. Standard stock solutions of compounds boiling below room temperature: Place about 9.8 mℓ methyl alcohol in a ground-glass-stoppered 10.0-mℓ volumetric flask. Let flask stand unstoppered about 10 min or until all alcohol-wetted surfaces have dried. Weigh to nearest 0.1 mg. Fill a valved gastight syringe with reference standard to 5.0-mℓ mark. Lower needle to 5 mm above methyl alcohol meniscus. Slowly inject gaseous reference standard into flask neck (the gas will dissolve rapidly in methyl alcohol). Immediately, reweigh to nearest 0.1 mg, dilute to volume, stopper, and mix by inverting flask several times. Store at 0°C or below. Calculate concentration in micrograms per microliter from net gain in weight. Stock standards prepared in methyl alcohol from gaseous reference standards stored with ground-glass seals generally are not stable for more than 1 week even when stored at 0°C. Preferably store such standards in glass vials with a TFE-lined screw cap. Fill vials at least 90 % full.

CAUTION: Because of toxicity of most organohalides, prepare primary dilutions in a hood. Preferably use a NIOSH/MESA-approved toxic gas respirator when handling high concentrations of such materials.

---

‡‡ Gas chromatographic methods are extremely sensitive to differences in materials used. Mention of specific products by "Standard Methods" does not preclude the use of other existing or as-yet-undeveloped products that give demonstrably equivalent results.

§§ Available from Supelco: Request Batch No. R-1579.

‖‖ Available from Waters Associates.

ENKA, N.V. Holland. Available from Applied Science Laboratories, P.O. Box 440, State College, Pa.

l. Calibration standards: From standard stock solutions prepare secondary dilutions in methyl alcohol such that a 20-μℓ injection into 100 mℓ organic-free water will generate a calibration standard that produces a response close (±10 %) to that of the samples (see ¶ (7)). Purge and analyze aqueous calibration standards in the same manner as samples. Aqueous standards are not stable; discard after 1 h. Inject standard stock solutions below the water surface, ideally near the flask bottom.

m. Quality check standard, 2.0 μg/ℓ: From standard stock solutions prepare a secondary dilution in methyl alcohol containing 10 ng/μℓ of each organohalide to be determined. Daily, inject 20.0 μℓ of this mixture into 100.0 mℓ organic-free water and analyze.

(4) Sampling

Collect all samples in duplicate. Fill sample bottles so that no air bubbles pass through sample as bottle is filled. Carefully seal bottles so that no air bubbles are entrapped. Maintain hermetic seal on sample bottle until analysis.

If free chlorine is present in sample add an inorganic chemical dechlorinating agent such as $NaSO_3$ or $Na_2S_2O_3$ to prevent continued formation of trihalomethanes. Add a stoichiometric excess of dechlorinating agent based on free chlorine residual measurements at time of sample collection. Store samples at 4°C until analysis. Analyze samples as soon as possible after collection because little is known about possible sample matrix effects.

(5) Conditioning Traps

Condition newly packed traps in desorption device overnight at 200°C with an inert gas flow of at least 20 mℓ/min. Vent trap effluent to the room; do not connect to analytical column. Before daily use, condition traps for 30 min while backflushing at 180°C.

(6) Procedure

a. Sample extraction: Warm sealed sample to room temperature (22°C) in a water bath. Adjust purge gas (nitrogen or helium) flow rate of 40 mℓ/min. Attach trap inlet to purging device. (On a valved system turn valve to purge-sorb position.) Remove plungers from two clean 5-mℓ syringes and attach a closed syringe valve to each syringe. Open sample bottle and carefully pour sample into one of the syringe barrels until it overflows. Replace syringe plunger and compress sample. Open syringe valve and vent any residual air while adjusting sample volume to 5.0 mℓ. Close valve. Fill and seal second syringe in an identical manner from same sample bottle. Reserve second syringe for a duplicate analysis, if needed. Attach 20-cm needle to first syringe. Open syringe valve and inject sample into purge chamber. Seal chamber by closing valve and purge sample for 11.0 min.

b. Analysis: As sample is being purged, cool chromatograph column oven to room temperature by opening oven door and turning off oven heater. After purging sample for 11.0 min, desorb trapped compounds into gas chromatograph by placing trap in desorber and attaching trap backflush flow fitting. On a valved system, turn valve to desorb position. Desorb for 4.0 min while heating trap to 180°C.

Empty and clean syringe, syringe valve, needle, and purging device as sample is being desorbed. Rinse purging device and sample introduction syringe twice with organic-free water between analyses. Whenever high concentrations are encountered (> 100 μg/ℓ) or when suspended solids are contained in the sample, remove purging device from instrument, wash with detergent solution, rinse in distilled water, and dry in an oven at 105°C.

After 4.0 min of desorption, disconnect trap backflush flow fitting from trap. On valved system turn valve back to purge-sorb position. Immediately, close oven door of gas chromatograph and heat column oven to initial operating temperature: 60°C for analytical column and 50°C for confirmatory column. Start collecting retention data and start strip-chart recorder as soon as column over heater is turned on. Program column according to ¶ (2) 1 above.

c. Calibration: Prepare calibration standards from standard stock solutions in organic-free water that are close to the unknown in composition and concentration. Use calibration standards of such concentration that 20 μℓ or less of the secondary dilution need be added to 100 mℓ of organic-free water to produce a standard at the same level as the unknown.

(7) Analytical Quality Control

Daily analyze the 2-μg/ℓ quality check standard before analyzing any samples. Calculate instrument status checks and lower limit of detection estimations from these data. In addition, use the 2-μg/ℓ quality check standard to estimate the concentration in samples. From this information determine appropriate standard dilutions to be made. Analyze at least one blank sample containing only organic-free water daily to monitor for potential interferences as described in ¶ (1) b.

Qualitative misidentifications are potential problems in gas chromatography. Whenever samples of unknown nature are analyzed, make duplicate analyses using the two recommended columns and whenever possible use mass spectrometric detection to provide unequivocal identification.

(8) Calculations

Compare sample peak height to standard peak height to calculate concentration:

$$\mu g/\ell = \frac{S}{P} \times C$$

where:

S = sample peak height,
P = standard peak height, and
C = concentration of standard, μg/ℓ.

Calculate and report limit of detection (LOD) for each normally reported sample component not detected for each analysis using the following criterion:

$$\text{LOD } (\mu g/\ell) = \frac{2\,(A \times ATT)}{(B \times ATT)}$$

where:

B = peak height (mm for 2-μg/ℓ quality check standard),
A = twice the noise level in millimeters at the exact retention time of the compound or the base-line displacement in millimeters from theoretical zero at the exact retention time for the compound. (Tracing these compounds through treatment processes is simplified by expressing concentrations in nanomoles per liter or smaller units. Regulatory reporting is in micrograms per liter.), and
ATT = attenuation factor.

(9) Precision and Accuracy

Single-laboratory accuracy and precision data were obtained by dosing 1-ℓ volumes of organic-free water with the organohalides listed in Table 53:1. The dosed water was used to fill vials that were sealed and stored under ambient conditions. Dosed samples were analyzed randomly over a period of 2 weeks. The data in Table 53:1 reflect errors due to the analytical procedure and storage.

(10) References

1. SYMONS, J.M., T.A. BELLAR, J.K. CARSWELL, J. DeMARCO, K.L. KROPP, G.C. POBECK, D.R. SEEGER, C.J. SLOCUM, B.I. SMITH & A.A. STEVENS. 1975. National organics reconnaissance survey for halogenated organics. J. Amer. Water Works Ass. 67:634.
2. BELLAR, T.A. & J.J. LICHTENBERG. 1974. The determination of volatile organic compounds in water at the μg/ℓ level in water by gas chromatography. J. Amer. Water Works Ass. 66:739.
3. DRESSMAN, R.C. & E.F. McFARREN. 1977. A sample bottle purging method for the determination of vinyl chloride in water at submicrogram per liter levels. J. Chromat. Sci. 15:69.

Table 53:1 Single-Operator Precision and Accuracy for Selected Organohalides

Compound	Dose μg/L	Number of Samples	Mean μg/L	Standard Deviation
Vinyl chloride	2.0	14	1.90	0.10
1,1-Dichloroethylene	2.0	13	2.03	0.13
trans 1,2-Dichloroethylene	2.0	14	1.96	0.10
1,1,2-Trichloroethylene	2.0	14	1.82	0.08
1,1,2,2-Tetrachloroethylene	2.0	14	1.90	0.10
Methylene chloride	1.07	12	1.11	0.23
Chloroform	1.19	12	1.21	0.14
Carbon tetrachloride	1.28	12	1.21	0.08
Bromodichloromethane	1.60	12	1.52	0.05
Chlorodibromomethane	1.96	12	1.91	0.09
Bromoform	2.31	12	2.33	0.16
1,2-Dichloroethane	1.00	12	1.00	0.04
Methylene chloride	10.7	8	10.0	0.89
Chloroform	11.9	8	11.3	0.16
Carbon tetrachloride	12.8	8	12.3	0.51
Bromodichloromethane	16.0	8	15.1	0.39
Chlorodibromomethane	19.6	8	19.1	0.70
Bromoform	23.1	8	22.5	1.38
1,2-Dichloroethane	10.0	8	9.57	0.24
Methylene chloride	107	11	96.3	10.9
Chloroform	119	11	105	7.9
Carbon tetrachloride	128	11	98.5	6.3
Bromodichloromethane	160	11	145	10.2
Chlorodibromomethane	196	11	185	10.6
Bromoform	231	11	223	16.3
1,2-Dichloroethane	100	11	92.5	3.9

2) Characteristics of Purge Trap Method

(1) No interaction occurs between precursor and residual chlorine.

(2) Hydrolysis of THM intermediate may have effect upon measured values depending on the mode of analysis as no prevention of hydrolysis is considered.

(3) The ion strength of sample has a little effect.

(4) Since operation is complicated, a special device is needed.

(5) Continuous gas chromatographic measurement is impossible only by one purge trap equipment.

(6) No solvent is needed.

(7) A variety of low boiling point organic chloric compounds can be measured simultaneously.

5-4 Characteristics of Head Space Method (Jordan)

(1) Interaction occurs between residual chlorine and precursor. This inhibition is able to eliminate by adding a thiosulfate and other reductant to remove residual chlorine into a sample.

(2) Hydrolysis occurs of THM intermediate. As the temperature of the head space analysis assembler of the gas chromatograph (Sigma 300) is set to 60°C., it would be impossible to prevent hydrolyzing of THM intermediate even if the pH of the sample is set to, say, 2. (As shown in Fig. 5, with pH 2, and the temperature of the assembler at a level below 40°C. there would be no hydrolysis of THM intermediate.)

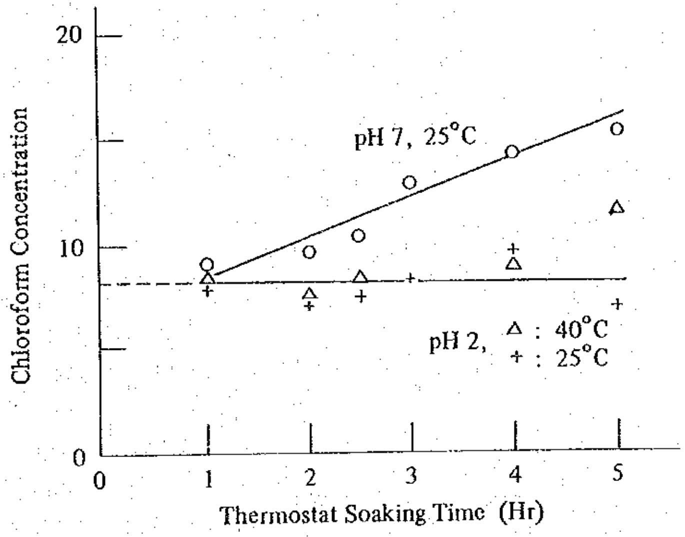


Fig. 5. Effect of Hydrolysis Inhibition on Chloroform Intermediate by Lowering pH

(3) Hardly affected by ion strength.

(4) High sensitivity for measuring.

(5) As it takes so long as 20 minutes for the head space assembler to rise in temperature, no continuous gas chromatrophic measurement is possible, therefore, inconvenient for analysing many samples.

5-5 Suggestion for Appropriate THM Analytical Method in Jordan

Since the tested water in Jordan contains much of bromine ion, the trihalomethane forming through chlorination contains a large proportion of bromine. The present analysis method employed in Jordan is not effective in preventing THM intermediate from hydrolyzing, therefore the measured values are high and widely variant.

As the result of careful consideration about the above problems, we are obliged to reach a conclusion in favor of the solvent extraction method described in 5-2 as the best practical analysis method. By this method, a THM extraction solvent could be taken easily by simple operation and then the solvent is injected into the gas chromatograph after detaching the head space assembler.